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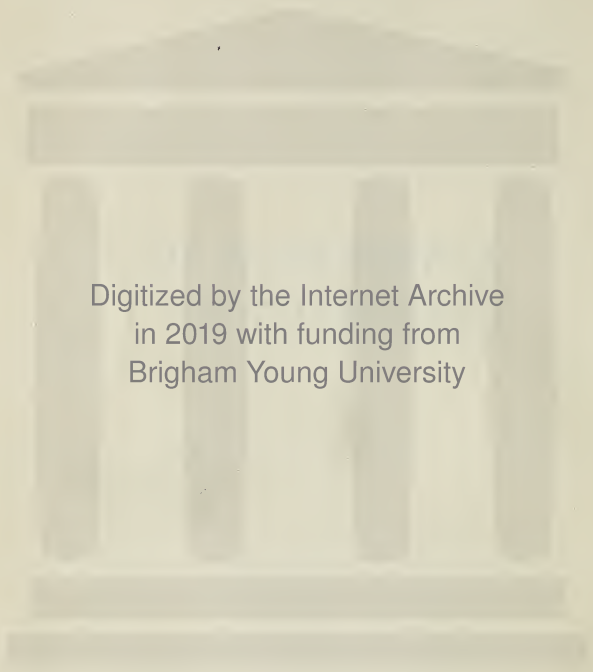
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**A FIRST BOOK IN
CHEMISTRY**



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A FIRST BOOK IN CHEMISTRY

BY

ROBERT H. BRADBURY, A.M., PH.D.

HEAD OF THE DEPARTMENT OF SCIENCE

SOUTH PHILADELPHIA HIGH SCHOOL



ILLUSTRATED

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TO
DR. EDWIN C. BROOME
SUPERINTENDENT OF PUBLIC SCHOOLS
IN THE CITY OF PHILADELPHIA
IN RECOGNITION OF HIS UNTIRING INTEREST
IN THE WORK AND WELFARE OF THE
TEACHERS OF THE CITY

PREFACE

This book follows the order of topics which has become standard in chemical teaching. I have aimed to obtain clearness of statement and simplicity of presentation and to interest the student while, at the same time, providing the opportunity to obtain information of permanent value. The industrial side of chemistry and its practical applications in the home are treated with unusual fullness.

The relation of chemistry to the civic community, to the farm, to the household, and to the manifold activities of the individual man and woman, is so intimate that almost all students approach the subject with an eager desire to learn about it. On account of the important part played by the chemist in the Great War, the interest in the science is now far more widespread and intense than ever before. I trust that this book may aid the teacher in his difficult but pleasant task of gratifying the curiosity of the many students who desire to know, not only what chemistry is, but what it has done for mankind.

The text meets completely the requirements of the various syllabi that teachers preparing students for college are obliged to consider.

Prof. A. L. Carey of the South Philadelphia High School for Boys has read both the manuscript and the galley proofs.

I am indebted to Miss May L. Laramy of the William Penn High School for a number of constructive suggestions growing out of her careful reading of the proof.

A separate volume containing the laboratory work is in preparation.

R. H. B.

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A FIRST BOOK IN CHEMISTRY

INTRODUCTION

THE METRIC SYSTEM AND THE CENTIGRADE SCALE

THE METRIC SYSTEM¹

Length. The metric unit of length is the **meter** (in French, *mètre*), which is almost 1.1 yards. More exactly, 1 meter (m.) = 39.37 in., or 1.094 yards. The door of the schoolroom is probably about a meter in width.

Corresponding in use to our mile is the **kilometer**, which is 1,000 meters, or a little more than three-fifths of a mile. More exactly, 1 kilometer (km.) = 0.62 mile. A kilometer is about 10 minutes' brisk walk.

The **centimeter** (cm.), which is $\frac{1}{100}$ of a meter, corresponds in use to the inch. It equals nearly two-fifths of an inch (1 centimeter = 0.39 in.). The diameter of the nail of the little finger is usually about a centimeter. The nickel coin is a trifle more than 2 cm. in diameter.

The **millimeter** is $\frac{1}{1000}$ of the meter or $\frac{1}{10}$ of the centimeter. It is about $\frac{1}{25}$ of an inch. More exactly, 1 millimeter (mm.) = 0.039 in. A dime somewhat worn in circulation is about 1 mm. thick. When an object is smaller than a millimeter in diameter, most persons, in examining it, find it desirable to use a lens.

¹ The detailed study of the metric system belongs to physics. The object of the present summary is merely to familiarize the student with the units constantly employed in chemical work.

Volume. The metric unit of volume is the volume of a cube of which the edge is 1 cm. long. It is called, therefore, the **cubic centimeter** (c.c.). A teaspoonful is about 7 c.c., and a teacup holds about 200 c.c. The small test tubes used in the laboratory hold about 30 c.c. There are 20 to 30 drops in a cubic centimeter.

Capacity. The metric unit of capacity is the **liter** (in French, *litre*), which is the volume of a cube of which the edge is 10 cm., or 3.93 in., long. It contains, therefore, 1,000 c.c. It equals almost exactly $\frac{9}{10}$ of a quart.

Weight. The metric unit of weight is the **gram** (in French, *gramme*), which is the weight of 1 c.c. of water at the temperature at which water is densest. The nickel coin weighs just about 5 grams. A gram is a little less than $\frac{1}{28}$ of an ounce. More exactly, 1 gram = 0.0353 ounce.

The **kilogram** (kg.) is 1,000 grams, or about $2\frac{1}{2}$ lb. (1 kilogram = 2.204 lb.). Half a kilogram, therefore, corresponds approximately to a pound.

THE CENTIGRADE SCALE

The centigrade scale takes as its zero the melting point of ice. The boiling point of water is called 100 degrees, and the graduation is continued above 100° and below 0°.

All temperatures mentioned in this book are centigrade, except that in some cases the corresponding Fahrenheit temperature is added for comparison. In such cases the Fahrenheit temperature is indicated by the addition of the letter F. to the number of degrees.

The student is familiar with the Fahrenheit scale, but he may have had no opportunity to become accustomed to the centigrade scale. He will frequently desire, therefore, to translate centigrade temperatures into Fahrenheit in order to realize the meaning of the former. The following is a simple rule for converting centigrade temperatures into Fahrenheit:

Multiply the centigrade temperature by 2, subtract one-tenth from the product, and add 32.

For example. A bright red heat is $1,000^{\circ}$ C. What is the corresponding Fahrenheit temperature?

Multiply 1,000 by 2.....	2,000
Subtract one-tenth.....	200
	1,800
Add 32.....	$1,832^{\circ}$ F. (<i>ans.</i>)

The open-hearth steel furnace operates at a temperature of $1,500^{\circ}$ C., which is a bright white heat. What is the corresponding Fahrenheit temperature?

Multiply 1,500 by 2.....	3,000
Subtract one-tenth.....	300
	2,700
Add 32.....	$2,732^{\circ}$ F. (<i>ans.</i>)

The conversion table in the Appendix may also be employed.

DENSITY AND SPECIFIC GRAVITY

Density. The weight of 1 c.c. of a substance is called its **density**. Thus the statement that the density of sulphur is 2.07 means that a cubic centimeter of sulphur weighs 2.07 grams.

Specific gravity. The **specific gravity** of a solid or liquid is the weight of a definite volume of it compared with the *weight of the same volume of water at 15° C. taken as unity*. For practical purposes, the specific gravities of solids and liquids may be regarded as identical with their densities.

The specific gravities of *gases* are usually stated in terms of the weight of the same volume of *air* as unity. They are, therefore, numerically quite different from the *densities* of the same gases.

CHAPTER I

PHYSICAL AND CHEMICAL CHANGE

1. Substances. The metal *iron*, so indispensable to civilization, is used in many distinct forms, as, for instance, bar, sheet, wire, chain, and gauze. These forms, so different to the metal-worker and the machinist, are alike to the chemist, for they all consist of the same *substance*, iron.

In the same way sugar is employed in the household for various purposes in the forms of granulated, pulverized, and lump sugar, but there is no chemical difference among these materials, for all three consist of the same substance, *sugar*.

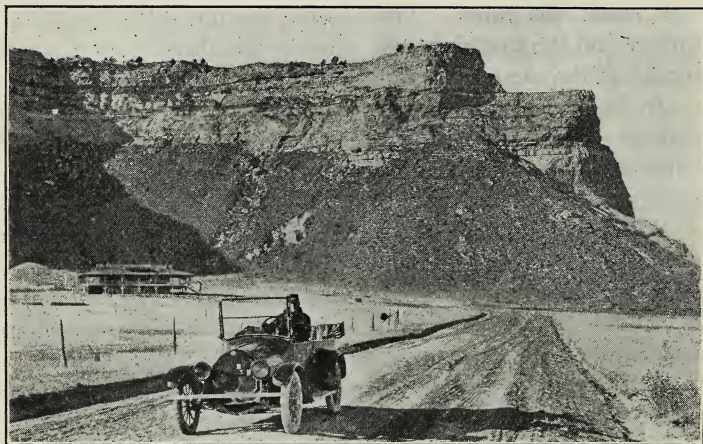
A *substance*, then, is a particular kind of matter, as iron, copper, sugar, salt, or sulphur. The same substance often occurs in nature, or in trade, in varieties or forms which seem to have little in common; yet to the chemist these forms are almost identical, for they are all made of the same material.

2. Changes in matter. Most of the materials that surround us are subject to *change*. Milk becomes sour, and meat decays. Copper exposed to air and water is slowly converted into a green rust, while iron under the same conditions changes more rapidly into a reddish-brown rust. Even the rocks, which may well claim to be the most permanent of all material things, slowly disintegrate under the ceaseless action of the weather, and thus form the soil of our planet.

PHYSICAL CHANGES

3. Changes in physical properties. Some of the changes in materials that take place of themselves, or are intentionally brought about, leave the *substance* unaffected. Thus, pulverized

sugar is made in the refinery by powdering the granulated variety, but both are sugar. A copper rod when heated becomes slightly longer than when cold. When, instead of heating the copper rod, we pass an electric current through it, the copper acquires a number of very interesting properties which it did not possess before, but the heated copper and the copper that is conducting the electric current are still copper. A steel bar when stroked with a magnet becomes itself a magnet, but the



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Fig. 1. Under the ceaseless action of the weather the rocks disintegrate to form soil.

steel is not converted into a new substance. A glass rod when rubbed with a silk handkerchief receives an electric charge and acquires the power of attracting light objects, such as fragments of paper, but the rod is still glass.

Changes like those just mentioned are called **physical changes**. It will be seen that a physical change does not alter the substance. It is a change of a *physical property* only, such as shape, size, color, temperature, electrical or magnetic condition. It is usually, though not always, easy to reverse a physical

change and return the object to its original state. Thus, if the copper rod is allowed to cool, it shrinks to its original length. When the electric current flowing through the copper is stopped, the new properties disappear. The electrified glass, left to itself, loses its electric charge and, with it, the power of attraction; and, by proper treatment, the magnetism of steel can be removed and the steel restored to its previous condition.

The study of physical changes is the province of the science of **physics**.

CHEMICAL CHANGES

There are changes of another kind which we must now proceed to explore.

4. The charring of sugar. A little sugar is placed in a dry test tube, and the tube is carefully heated (Fig. 1). The sugar melts and blackens, and a vapor possessing the peculiar odor of burnt sugar escapes. After the heating, charcoal is found in the bottom of the tube, while drops of a dark liquid cling to the inside surface of the upper portion. This liquid contains water and many other substances. It is clear that, in this experiment, the sugar has disappeared and new materials have been formed in its place.

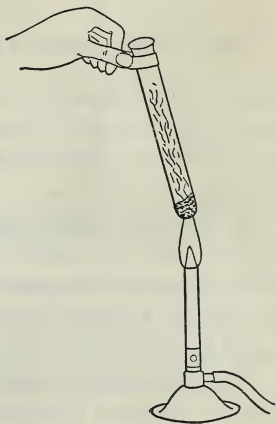


Fig. 2. The charring of sugar.

5. Heating copper in the air.

Let us now return to the copper rod, but instead of merely warming it enough to expand it, let us heat it nearly red hot for a considerable time (Fig. 2). It is necessary to hold the copper with a little pair of tongs called *forceps*, as copper is a good conductor of heat, and even the portions of the rod remote from the flame soon become quite hot.

Black scales slowly form on the surface of the hot copper. This new substance can be collected by holding the copper over a clean paper and tapping it gently with a pencil. More of the black material can be obtained, if desired, by heating the copper a second time. In fact, by heating often enough the copper could be completely transformed into the black

scales, though a very long time would be required to achieve this result.

For reasons we shall soon learn, the black substance is called by the chemist *copper oxide*. It proves, upon examination, to be unlike copper not only in color, but also in all its other properties. Thus, the copper is bright, metallic,

tough, and malleable, so that it can be easily rolled or hammered into thin foil, whereas the copper oxide is dull, earthy, and brittle, so that when hammered it merely becomes a finer powder.

6. Heating copper with sulphur. Some sulphur is heated in a dry test tube until it boils vigorously and the tube is filled with yellow sulphur vapor. A piece of thin sheet copper weighing exactly 4 grams is in readiness, and it is rolled up so that it will pass easily into the test tube.

When the roll of metal is picked up with forceps and plunged into the vapor of the boiling sulphur, the copper takes fire and burns completely in a few seconds, yielding a black solid not unlike copper oxide in appearance (Fig. 3). This black substance must consist of copper and sulphur; it is called, therefore, *copper sulphide*.

If the idea that the copper has united with the sulphur is correct, then the copper sulphide should weigh more than the

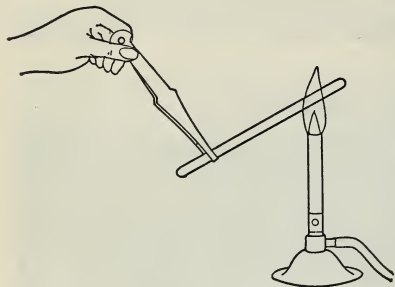


Fig. 3. Heating copper in the air.

copper did. As a matter of fact, when the roll is carefully withdrawn from the tube, without losing any of it, and taken to the balance, it is found to weigh *5 grams*. When copper burns in sulphur vapor, it unites always with one-fourth of its weight of sulphur; no matter what quantities of copper and of sulphur we may take, it is impossible to change this proportion.

7. The science of chemistry. It is evident that in the charring of sugar, in the production of copper oxide, and in the burning of copper in sulphur vapor, the materials with which we started the experiments have been changed into new substances. Changes such as these are **chemical changes**. Whereas in a physical change only *one* property of a material is usually concerned, in a chemical change *all* the properties undergo a complete transformation. It is usually, though not always, more difficult to reverse a chemical change than a physical change. Thus, the charcoal, the copper oxide, and the copper sulphide, when cold, show no tendency to return to the original state.

The study of chemical changes is the province of the science of **chemistry**. An important reason for studying chemical changes is that we may learn to control them and to apply them to purposes useful to mankind.

8. Heating metals in the air. It is an historical fact that the science of chemistry arose out of observations on the

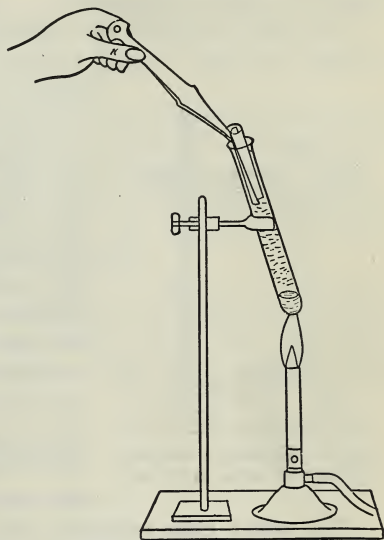


Fig. 4. Heating copper in sulphur vapor.

behavior of metals when heated and attempts to explain the chemical changes that occurred. It will be of interest, therefore, to inquire whether the other familiar metals behave in the same manner as copper when heated in such a way that the air has free access to the metal

In order to obtain an answer to this question, it is convenient to heat a small weighed quantity of the powdered metal in a porcelain crucible, and to reweigh after any change that occurs is complete (Fig. 5). Working on to this plan, we find that there are a few metals that are unaffected by heating to redness in the air, for they retain their lustre and are unchanged in weight. These belong to the class of the so-called "*noble*" or "*precious*" metals, which includes gold, silver, and platinum, and some others less well known. These metals occur somewhat rarely in nature, and they are, therefore, rather expensive.

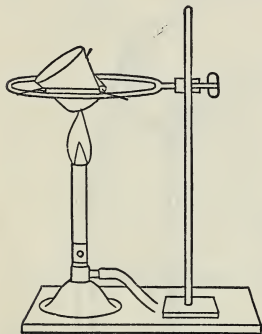


Fig. 5. Heating a weighed quantity of metal in the air.

The other class comprises the cheaper metals, sometimes called the "*base*" metals, such as iron, copper, lead, zinc, tin, aluminum, and magnesium. These behave like copper when heated in the crucible—that is, they are converted into lustreless, earthy masses in which all trace of the properties of the metal is lost. These products are called **oxides**, and the change of a metal into its oxide is always accompanied by a gain in weight. Thus, when lead is heated, it changes slowly into a dull-yellow powder called *lead oxide*; the gain in weight in the complete change is always one-thirteenth of the weight of the lead taken, so that 13 grams of lead yield 14 grams of lead oxide. The metal magnesium burns brilliantly when heated. The product is a pure-white powder of *magnesium oxide*, commonly called *magnesia*. The increase in weight is always two-thirds of the

weight of the magnesium taken, so that 3 grams of magnesium yield 5 grams of magnesia when the change is complete.

SUMMARY

A **substance** is a particular kind of matter, such as sugar, salt, sulphur, iron, or copper.

Changes in matter are of two kinds:

1. Those in which one or more of the physical properties of a material are altered but without changing it into another substance. These are called **physical changes**.

2. Those in which all the properties of a material are altered simultaneously, so that one or more new substances are produced. These are called **chemical changes**.

When heated in the air, the *precious metals* are unchanged, but the *common metals* are converted into lustreless, earthy masses called *oxides*. The metal must unite with something from the air in this process, for the oxide always weighs more than the metal used.

EXERCISES

1. What is meant by the term *substance*?

2. State the distinction between physical and chemical changes.

3. Classify into physical and chemical changes the following: the souring of milk; the freezing of water; the boiling of water; the burning of coal, wood, kerosene, and a candle; the decay of fallen leaves; the coinage of gold; the lighting of an incandescent electric lamp; the lighting of a Welsbach-mantle gas light; the change of cider into vinegar; the formation of the dark crust on bread during baking.

4. Classify into physical and chemical changes, with reasons, the heating in air of the following metals: gold, copper, lead, platinum, silver, and magnesium.

5. How much will 207 grams of lead gain in weight when heated till the chemical change is complete? What will be the weight of the lead oxide?

6. How many grams of magnesium oxide can be obtained by heating 24 grams of magnesium?

7. What are some of the products when sugar is charred? Is this a physical or a chemical change? What kind of change occurs when sugar is stirred with water? Why?

8. Name three physical and three chemical changes not mentioned in this chapter.

9. Which are the more useful, the "base" or the "noble" metals? To which class does the most useful metal of all belong? Why?

10. Are most of the changes that occur in cooking physical or chemical? Is the freezing of ice cream a physical or a chemical process?

CHAPTER II

THE ACTION OF AIR ON HOT METALS

9. Effect of heat in absence of air. The experiments of the preceding chapter have shown that when any of the common metals is heated in the air, it is converted into its oxide, the properties of which are totally different from those of the metal. The fact that this change always takes place with *increase in weight* indicates strongly that the metal unites with some substance derived from the air.

Theoretically, the simplest way to test this conclusion would be to heat the metal in a vacuum to ascertain whether or not the change to oxide occurs under these conditions. This is done in the *tungsten lamp*, often called the "Mazda" lamp (Fig. 6), so widely employed for electric lighting. The Mazda lamp consists of a fine wire of *tungsten* supported in a vacuum. The wire is heated to whiteness by the passage of an electric current. Tungsten is a metal which, when heated *in the air*, changes into a yellow oxide. If, while a Mazda lamp is burning, the glass be perforated to admit air, the hot tungsten wire is instantly changed to tungsten oxide, and the lamp is spoiled. Yet in a vacuum the wire may glow for years without the formation of a trace of oxide. This leaves little doubt that the air is essential to the change.

10. Heating a folded piece of copper. A bright piece of sheet copper is rolled up, the roll flattened with pliers, and the ends of the roll squeezed shut and bent over (Fig. 7). The

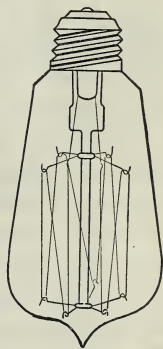


Fig. 6. Tungsten incandescent lamp.

metal, held in forceps, is then heated. It is clear that the air has free access to the outside of the roll, while the copper inside the roll, though heated to redness, is protected from the

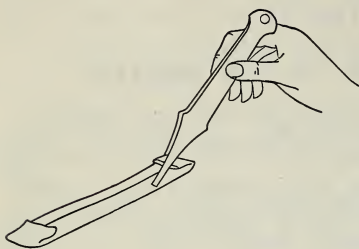


Fig. 7. Sheet copper folded for heating in air.

air. When the exterior is coated with black copper oxide, the roll is allowed to cool and opened. *The inside surface of the copper is as bright as it was before the roll was heated.* We conclude, therefore, that the air is necessary to the change of metals into their oxides, for heat alone fails to produce the result.

11. Heating powdered iron in air. The next problem is to determine whether *all* of the air or only a *portion* of it is concerned in the conversion of a metal into its oxide. The experiment shown in Figure 8 yields an answer to this important question. A horseshoe magnet is hung on a glass rod in a bell-shaped glass jar. Bits of rubber tubing, slipped over the ends of the rod and crowded against the jar, hold the rod in place. The open end of the jar is immersed in water in a trough and rests upon a shelf. A supply of iron powder clings to the poles of the magnet. The burning of the iron is started by a red-hot iron wire, introduced through the neck of the jar, and then the stopper is replaced.

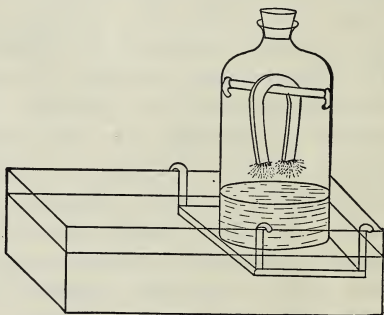


Fig. 8. Heating powdered iron in a limited volume of air.

The iron burns for a time, but the burning ceases much sooner than it would have done in the open air. The level of the water in the jar rises until about one-fifth of the jar is filled with water. The jar is transferred from the shelf to the bottom of the trough, the stopper is removed, and a burning wooden splint is inserted. The flame is extinguished at once.

From this experiment we conclude that only a portion of the air is concerned in the transformation of a metal into its oxide. Further, the material in the air that converts a metal into its oxide is also the *cause* of the *ordinary burning* of wood, candles, etc. The air, then, contains about one-fifth of its bulk of an active gas which unites with metals and causes candles, fuel, etc., to burn. About four-fifths of the air consists of an *inactive* material which takes no part in these processes. The active substance, of which the air contains about one-fifth by volume, is **oxygen**; the rather inert gas, of which the air contains nearly four-fifths, is called **nitrogen**.

12. Percentage composition of air. More exact information about the proportions of oxygen and nitrogen in the air

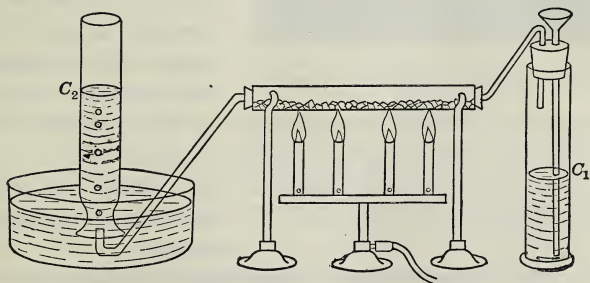


Fig. 9. Apparatus for determining the composition of air by volume.

can be obtained by passing a measured volume of air through a column of heated copper clippings, which removes the oxygen. The nitrogen, which passes through the copper without being absorbed, is collected over water in a graduated vessel and measured. The apparatus is shown in Figure 9. C_1 is a grad-

uated cylinder which is full of air when the experiment is begun. C_2 is a similar cylinder full of water. A liter of water is allowed to drop into C_1 , the displaced air is forced through a column of hot copper clippings, and the nitrogen passes on into C_2 . If the work has been well done, 790 c.c. of gas will be found in C_2 .

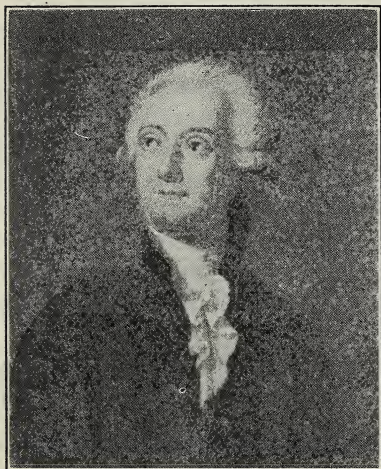


FIG. 10. ANTOINE LAURENT LAVOISIER
(1743-1794).

French scientist, "the founder of modern chemistry"; investigated the composition of air and of water, explained the phenomena of combustion, and advanced the theory of the indestructibility of matter. He was victim of the French Revolution.

If this gas be made to pass over the hot copper a second time, there is no further loss in volume. Like the gas obtained by the burning of powdered iron, the gas that collects in C_2 immediately extinguishes the flame of a burning splint or taper.

Since we began with 1,000 c.c. of air, 1,000-790, or 210 c.c. of gas must have combined with the copper. Therefore the air contains 21 per cent of oxygen by volume. Of the remaining 79 per cent, by far the greater part is nitrogen, but, as we shall see, small quantities of other gases are present in the air.

13. The "twelve-days' experiment" of Lavoisier. How could we proceed to obtain *pure* oxygen, entirely free from nitrogen? One possibility would be to heat a metal in the air until it was changed into its oxide, and then, in a second experiment, to heat the oxide to a higher temperature to break it up into metal and oxygen, the oxygen being collected over water or in some other suitable way. This was done in 1775 by the

great French chemist *Lavoisier*, the founder of modern chemistry. On account of the length of time required to carry it out, the investigation is often called the "twelve-days' experiment."

The metal employed by Lavoisier was *mercury*, often called "quicksilver," the familiar liquid metal used in thermometers. His apparatus is shown in Figure 11. The retort containing the mercury was heated in a charcoal stove. The glass bell jar dipped into mercury in a dish in order to exclude the external air. Since the jar and the retort communicated, the contained air passed freely back and forth, and all the air in both took part in the process. The total volume of air in the apparatus was 40 cu. in.

During the heating a red powder of *mercuric oxide* appeared floating on the mercury in the retort, and that some of the air was absorbed was shown by the rise of the mercury in the jar. After 12 days' heating the level of the mercury ceased to rise, and Lavoisier concluded that all the oxygen of the air in the apparatus had united with the mercury. Eight cubic inches of the total volume of 40 cu. in. of air had been displaced by mercury.

Lavoisier now removed the mercuric oxide and heated it strongly. The 8 cu. in. that had been lost were recovered in the form of a colorless gas in which a candle burned much more brilliantly than in air. This gas was *oxygen*.

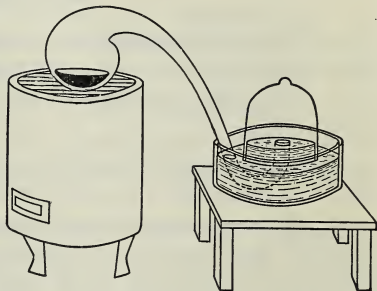


Fig. 11. Apparatus of Lavoisier's "twelve-days' experiment."

SUMMARY

When iron powder is burned in a confined volume of air, one-fifth of the air unites with the iron, and the remaining gas extinguishes flame.

A measured liter of air when passed over hot copper loses 21 per cent by volume, which unites with the copper. The gas that unites with the copper is **oxygen**. The gas that is not taken up by the copper is chiefly **nitrogen**. A burning candle is quenched in nitrogen as though dipped into water.

Lavoisier obtained oxygen from the air by first causing the oxygen to combine with mercury, and then strongly heating the mercuric oxide.

EXERCISES

1. What is the experimental proof that the same constituent of the air that converts iron into iron oxide also causes a candle to burn?

2. How could you determine the percentage by volume of oxygen in air?

3. In the experiment shown in Figure 9 the copper turns black. Why? In which end of the tube would the blackening first appear?

4. The percentage of oxygen in air *by volume* is 21, whereas *by weight* the percentage is 23. Explain exactly what is meant by these statements. Which must be the denser gas, oxygen or nitrogen?

5. In what way did Lavoisier obtain oxygen from air?

6. Classify into physical and chemical changes the following: the boiling of mercury in a vacuum, as in the mercury-vapor lamp; the effect of heating mercury in air, as in Lavoisier's experiment; the effect of heat upon the *interior* of a rolled-up sheet of copper; the effect of heat and air upon the *exterior* of the same roll of copper; the effect of heating iron in air.

7. Note that the change of mercury when heated in air is *reversible*. If this had not been the case, could Lavoisier have obtained oxygen from the air in this way?

8. Suppose that the air were suddenly changed to pure oxygen. What would be some of the noticeable effects?

9. Compare oxygen with nitrogen as completely as possible.

10. Would it be easy to remove the *nitrogen* from air, leaving gaseous oxygen behind? Why did all the investigators follow the opposite course?

CHAPTER III

ELEMENTS, COMPOUNDS, AND MIXTURES

14. Elements. Although it may be preserved for an unlimited time in the cold, mercuric oxide when heated promptly breaks up into mercury and oxygen. We shall meet with numerous examples of this power of high temperatures to split compound substances into their constituents. Both in the laboratory and in the chemical works heat is constantly employed for this purpose.

A problem now suggests itself. How far can we carry this splitting or analyzing process? If the mercury, for instance, were confined so that it could not boil away and were heated to a white heat or beyond, would it be resolved into still simpler substances?

This is a most important question. In the effort to answer it, mercury has been subjected, not only to high temperatures, but also to light, mechanical disturbance, and the electric current, for these, like heat, often bring about the breaking up of compound substances. Such attempts have always failed. The only way to change mercury into anything else is to proceed as Lavoisier did when he made it combine with the oxygen of the air, that is, to *add something to the mercury*. In this way, by using many other materials as well as oxygen, a great many compound substances containing mercury have been prepared, but not the slightest evidence of any breaking up of the mercury has ever been obtained. Substances made by such processes weigh *more* than the mercury used. Plainly, if the mercury were broken up, each constituent would weigh *less* than the mercury itself.

A substance that, like mercury, has hitherto resisted all attempts to convert it into simpler materials is called an **element**. Not only mercury, but also all the other metals—for instance, iron, copper, tin, lead, zinc, nickel, gold, silver, and platinum—are elements. About sixty *metallic* elements are known. About twenty *non-metallic* elements have been discovered. Thus far we have encountered only three of the non-metallic elements—oxygen, nitrogen, and sulphur.

15. Table of the elements. An alphabetical list of the elements is given in the Appendix. Eighty-three, all that are known with certainty, are included. For reasons that cannot be discussed here, it is not likely that many elements remain unknown. The total number possible seems to be 92, and since more than 80 are known, less than a dozen elements remain to be discovered. The names of the more abundant and important elements—the ones that we shall study in detail—are printed in **boldface** in the table.

16. Chemical symbols. Following the name of each element in the table is its **symbol**, an abbreviation of its name. Frequently the symbol is the first letter of the name. Thus, the symbol of *oxygen* is **O**, of *sulphur* **S**, and of *nitrogen* **N**. In other cases an additional letter, often the second letter of the name, is added. This is true of the symbols of *silicon* (**Si**) and of *nickel* (**Ni**). Thus the danger of confusing *silicon* with *sulphur* or *nickel* with *nitrogen* is avoided.

By international agreement among scientists, the same chemical symbols are used in all countries regardless of differences in language. When the name of an element begins with a different letter in different languages, the symbol is derived from the Latin name of the element. Thus, the symbol of *gold* (**Au**) is formed from the Latin *aurum*. In the same way the symbol of *mercury* (**Hg**) is derived from the Latin *hydrargyrum*.

The symbol of an element stands for more than the name. It represents also a certain definite quantity by weight, always

the same for the same element. Thus O means 16 *parts* by weight of oxygen; S, 32 *parts* by weight of sulphur; and Hg, 200 *parts* by weight of mercury. For each element the number of parts by weight represented by the symbol is given in the table in the column headed "Exact Values." For the more important elements "Approximate Values" are given in the fourth column of the table. The approximate values should be used in solving all problems.

17. The elements in nature. The elements known to us are not restricted to the earth alone. Numerous meteors have been carefully examined but no new element has been discovered in them. They consist of iron, nickel, and other substances well known to the chemist. By investigating, by means of an instrument known as the *spectroscope*, the *light* that comes to us from the heavenly bodies, it is possible to analyze them almost as precisely as if we had samples of them in the laboratory. Sun, stars, comets, and nebulae prove to consist of the same elements already familiar in terrestrial matter.

The following table gives a list of the more common elements in the order of their abundance in nature. The table, which is based upon thousands of analyses, has been carefully computed by Professor Clarke. It must be remembered, however, that our knowledge of the earth's crust extends only to a layer about 5 miles in depth, which is a mere film compared with the diameter of the earth. In the deep interior the relative composition is probably entirely different.

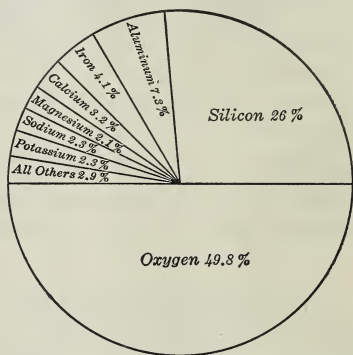


Fig. 12. Percentage composition of the earth's crust.

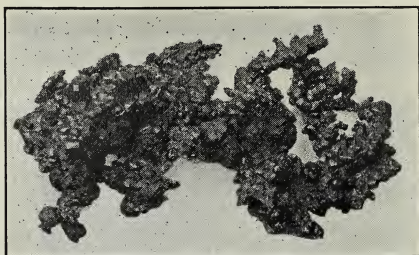
COMPARATIVE ABUNDANCE OF THE ELEMENTS IN NATURE

Elements (in Order of Abundance)	Percentage Composition of the Solid Crust of the Earth	Percentage Composition of Sea Water	Percentage Composition of the Earth's Crust Including the Ocean and the Atmosphere
Oxygen.....	47.17	85.79	49.85
Silicon.....	28.00		26.03
Aluminum.....	7.84		7.28
Iron.....	4.44		4.12
Calcium.....	3.42	0.05	3.18
Potassium.....	2.49	0.04	2.33
Sodium.....	2.43	1.14	2.33
Magnesium.....	2.27	0.14	2.11
Hydrogen.....	0.23	10.67	0.97
Titanium.....	0.44		0.41
Carbon.....	0.19	0.002	0.19
Chlorine.....	0.06	2.07	0.20

The student will notice that oxygen makes up one-half the crust of the earth, and silicon one-fourth. This is a striking illustration of the *inequality* in the abundance of the elements. It will also be seen that most of the elements are not listed in the table at all. The reason for this is that none of the missing elements makes up as much as one-tenth of 1 per cent of the earth's crust, and that all of them together sum up to only a small fraction of 1 per cent. Yet among the elements absent from the table are such familiar and important substances as lead, copper, tin, and zinc. Even nitrogen, without which no form of life upon the earth would be possible, does not find a place in the list.

18. Native elements. Gold occurs in the Klondike and elsewhere in the form of yellow, glittering grains disseminated through the sands in the beds of brooks. This is called **native**

gold. The term "native" means that the element occurs in nature in the free state, that is, not in chemical union with some other element. Native gold is the most important source of the gold of commerce. *Native copper* occurs in quartz veins in northern Michigan, where large quantities of it are mined, but copper also occurs in compound substances in which the presence of copper would never be revealed by mere inspection, even with a microscope. Thus, copper sulphide, which occurs at Butte, Montana, and many other places, is an important source of the metal. To ores of this character the term "native copper" is not applied.



Courtesy of the American Museum of Natural History.

Fig. 13. Native copper as it occurs in Michigan ore.

The figures in the table just given refer chiefly to the occurrence of elements in nature in the form of compound substances. Native elements play only an unimportant part in the structure of the crust of the earth.

19. The elements of the human body. The average composition of the human body is given in the following table, which is due to Professor Sherman:

COMPOSITION OF THE HUMAN BODY

Per cent		Per cent		Per cent	
Oxygen.....	65	Phosphorus...	1.0	Magnesium...	0.05
Carbon.....	18	Potassium....	0.35	Iron.....	0.004
Hydrogen.....	10	Sulphur.....	0.25	Iodine.....	trace
Nitrogen.....	3	Sodium.....	0.15	Fluorine.....	trace
Calcium.....	2	Chlorine.....	0.15	Silicon.....	trace

The 15 elements of this table are the most important

constituents, not only of the human body, but also of all living organisms, both animals and plants. Other elements are found in living matter, and may be essential to vital processes, but they are present only in traces.

20. Transmutation of elements. To find some way of transmuting the cheaper metals, like lead, copper, and tin,

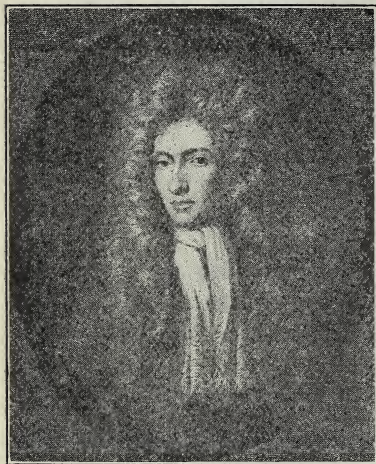


FIG. 14. ROBERT BOYLE (1627-1691).

Irish scientist; defined the nature of the elements and discovered the relation between pressure and volume in gases expressed in what is known as Boyle's Law.

Irish chemist *Robert Boyle*, in 1661, extended this idea from gold to the other elements. Denouncing alchemy as a delusion, he stated with perfect clearness the modern conception of the elements as substances which we may cause to enter into combination, but which we cannot transform into one another.

This statement still holds true to-day, but it would be a mistake to conclude from it that each of the elements is a simple form of matter having no relation to any other element.

into gold was one of the chief pursuits of the mediæval chemical science known as alchemy. This endeavor began in Egypt, whence it was carried to Spain by the Arabs. Thence it penetrated all parts of Europe, where it flourished for centuries, and thousands of men wasted their lives in experiments which were always fruitless. Out of innumerable failures there gradually emerged the conviction that *transmutation is impossible*, and that in order to obtain gold, one must start the experiment with some material that contains it. The famous

Twentieth-century science has proved beyond question that all of the elements are composed of the same materials, differently arranged. Moreover, while it is still true that chemists cannot intentionally *bring about* transmutation of the elements, yet well authenticated instances are on record in which elements *of themselves* have slowly changed into other elements. We shall return to this interesting subject later.

21. Compounds and mixtures. *Mercuric oxide* is a brick-red powder, the appearance of which would never suggest that it is composed of a silvery, liquid metal and a colorless gas. Even under a powerful microscope it still appears a uniform red substance; in other words, it is *homogeneous*. Its composition is always the same, for a fixed weight of mercury combines with the same weight of oxygen no matter how often the experiment is repeated. The same statements hold good for the oxides of the other metals. The properties of the oxides are altogether distinct from those of the metals and of oxygen, and each oxide has an invariable composition. Copper sulphide, also, we have found to be a black solid in which the presence of copper or of sulphur would not be suspected. The composition of copper sulphide is always the same, for copper always combines with one-fourth of its weight of sulphur.

*Substances that are homogeneous, that possess properties different from those of their constituents, and that possess a fixed composition are called **chemical compounds**.*

By shaking copper filings with sulphur it is easy to obtain a material containing both, but this is not a compound, for it is not homogeneous, its properties are simply those of copper and of sulphur, and its composition can be varied at will. Such a material is a **mixture**. The terms *mixture* and *compound* have precise meanings in chemistry, and they should never be confused.

Such a mixture of copper and sulphur, however, can easily be converted into a chemical compound. All that is necessary is to heat the test tube containing the mixture gently at one

point to start the chemical change. The mass glows brightly, showing that much heat is evolved. *Heat is usually generated when two elements unite to form a compound.*

On breaking the tube we find a black, homogeneous mass of copper sulphide, the properties of which bear no resemblance to those of the elements of which it is composed. The distinctions between compounds and mixtures exemplified in this experiment are stated in the following table:

DISTINCTIONS BETWEEN MIXTURES AND COMPOUNDS

Distinction in	Mixtures	Compounds
1. APPEARANCE	Not homogeneous	Homogeneous
2. SEPARATION	Easy by methods based upon the different physical properties of the constituents	Impossible by methods based upon the physical properties of the constituents
3. PROPERTIES	Can be predicted from those of the constituents	Have no relation to those of the constituents
4. HEAT-PRODUCTION DURING FORMATION	None	Usually much heat given out. Sometimes heat absorbed
5. PROPORTIONS OF THE CONSTITUENTS	Can be varied at will	Always the same in the same compound

The fact that *the composition of the same chemical compound is always the same* is called the **law of definite proportions**.

The second distinction in the table will be made clearer by an example. Imagine a pound of granulated sugar to be thoroughly mixed with a pound of sand. This mixture could be separated by picking out the sugar grains with fine forceps,

leaving the sand. Or, we could treat the mixture with *water*, which would dissolve the sugar, the sand remaining. The sugar could be obtained again by boiling away the water. Both of these methods are based upon the fact that the physical properties of sugar are different from those of sand. Such methods fail to work when applied to chemical compounds, because a compound is *one substance*, and as such has its own individual properties.

22. The conservation of matter. We have seen that when Lavoisier heated mercury in a closed vessel with 40 cu. in. of air, 8 cu. in. of oxygen entered into combination with the mercury and disappeared. When he afterward heated the mercuric oxide intensely, the 8 cu. in. of oxygen was recovered. In another classic experiment (1774) Lavoisier placed a weighed quantity of tin in a flask, which he then sealed by melting the neck with a flame, so that nothing could either enter or leave it. The flask, after being weighed, was heated for some days, during which the tin was converted into a white powder of tin oxide. The weight of the flask, however, remained the same. Hence, the weight of the tin and the oxygen was the same after they had entered into chemical combination as before; the chemical change that had occurred in the flask had neither created nor destroyed any matter. When the flask was opened, air rushed into it, and now the balance showed a decided increase in weight. Lavoisier removed the tin oxide, and found that it weighed more than the tin. The difference was equal to the increase in weight of the flask when opened.

On the basis of this and other similar experiments, Lavoisier stated clearly what is now known as the **law of the conservation of matter**. Matter, though its form is changed, is not created or destroyed in chemical reactions. The weight of a sealed vessel is not changed by a chemical process that takes place within it. Let A and B be two elements that unite to form a compound AB . Then the weight of AB will equal the sum of the weights of A and B that united. This is what

occurred in Lavoisier's experiment with the tin. This kind of chemical change is called **combination**.

The separation of a compound into its elements is called **decomposition**. If the compound AB decomposes into A and B , the sum of the weights of A and B produced will equal the weight of AB used. Thus, when mercuric oxide is heated, the sum of the weights of the mercury and of the oxygen produced equals the weight of the mercuric oxide.

The law of the conservation of matter seems to hold true, not only on the earth, but throughout the universe. On the sun physical and chemical processes are continually occurring on a gigantic scale. Yet the quantity of matter in the sun remains the same, for any change in its mass would affect the force with which the sun attracts the planets, and would cause alterations in their motions which the telescope would at once detect.

SUMMARY

Analysis of the different materials in the crust of the earth reaches its limit in the **elements**, substances which resist attempts to decompose them. About 80 elements are known with certainty.

About twenty of the known elements are *non-metals*; the rest are *metals*.

Only a few elements remain to be discovered, the total number possible being but 92.

Two, or at most three, primary materials make up all the elements.

The **symbol** of an element is often the first letter of its name. For many of the elements a second small letter is added to avoid confusion.

The symbol represents a *definite quantity by weight*, which is always the same for the same element.

The elements are unequally abundant in nature. Eight of them make up 99 per cent of the crust of the earth. These, in

order of decreasing abundance, are: oxygen, silicon, aluminum, iron, calcium, magnesium, sodium, and potassium.

Only 15 elements are found in important quantities in the bodies of animals and plants.

Chemists have found it impossible to achieve transmutation of the elements. However, there are well known cases in which elements *of their own accord* slowly change into other elements.

No chemical change in the interior of a sealed vessel will produce the slightest change in the total weight. Matter is indestructible, and it cannot be created. This is the **law of the conservation of matter**.

When two elements unite to form a compound, the properties of the elements, with the exception of weight, are completely lost. The compound has its own properties, which have no relation to those of the elements composing it.

The percentage composition of the same chemical compound is always the same. This is called the **law of definite proportions**.

The properties of a **mixture** are merely those of its constituents. A mixture can be made in any desired proportions.

EXERCISES

1. What is meant by the term *element*?
2. What is a *native* element? Mention some elements that occur mainly native. Mention several that are found chiefly in compounds.
3. Distinguish clearly between *compound* and *mixture*.
4. State the *law of the conservation of matter*. Describe Lavoisier's experiment which demonstrated this law.
5. What is the astronomical proof of the law of the conservation of matter?
6. State the *law of definite proportions*. To what class of substances does it apply?
7. What is *alchemy*? What was the main result of the labors of the alchemists?
8. Is it quite correct to say that the symbol *Hg* means mercury? How much mercury is indicated by the symbol of the element?

9. How many different symbols are needed in chemistry? Why?

10. Enumerate all the distinctions you can think of between a *metal*, like gold, and a *non-metal*, like sulphur. How do the two differ in appearance? In toughness? In behavior under the hammer?

11. Name eight elements that together make up almost the whole of the crust of the earth.

12. Name six elements that together make up at least 99 per cent of the weight of the human body.

13. Using a large dictionary, define *homogeneous* and *heterogeneous*. Are *elements* homogeneous? Are *compounds*? How about mixtures?

14. Beginners in chemistry often inquire why mercuric oxide is *red*, although neither mercury nor oxygen has any color. Criticize this question. Can you answer it? Could anyone answer it?

15. Could you prepare (a) a compound from elements, (b) an element from a compound, (c) an element from another element?

16. Mention six elements that were known to you before beginning the study of chemistry.

17. Classify the following into compounds and mixtures: varnish, salt, sea water, table sirup, sugar, paint, mortar, turbid water, pure water, milk.

CHAPTER IV

OXYGEN

23. Importance of oxygen. Because of its great importance and abundance, oxygen offers the natural beginning for a systematic study of the elements. It constitutes about one-half of the crust of the earth; that is to say, the common rocks, such as granite, sandstone, limestone, and basalt, contain about half their weight of oxygen. It constitutes eight-ninths by weight of water, which is a compound of oxygen and another invisible gas, *hydrogen*. Two-thirds of the weight of the human body, and of the bodies of animals in general, is composed of oxygen, and it also forms about half the weight of the substance of plants.

These statements all refer to oxygen in chemical combination. Oxygen in the *free* state makes up more than one-fifth of the air by volume. This free oxygen of the air is essential to the life of most plants and of all animals. No form of animal life is able to obtain oxygen for its vital

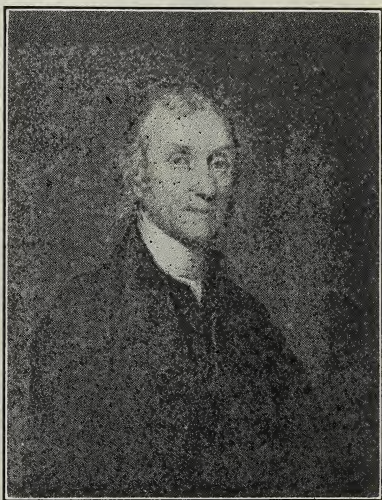


FIG. 15. JOSEPH PRIESTLEY (1733–1804).

English clergyman and philosopher; discovered oxygen and other gases and explained the cycle of oxygen in nature. He spent the last decade of his life in Pennsylvania.

processes from oxygen compounds. Fish, for example, cannot make use of the oxygen that is in combination with hydrogen in water. Their life is supported by a little free oxygen from the air, which dissolves in the water and thus reaches their respiratory organs.

24. Discovery. Oxygen was discovered on August 1, 1774, by Dr. Joseph Priestley, an English clergyman, who obtained it

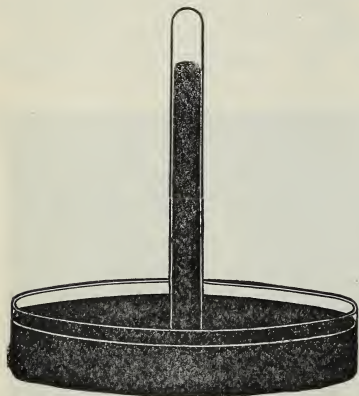


Fig. 16. Apparatus with which Priestley discovered oxygen.

by heating mercuric oxide. His apparatus is shown in Figure 16. The mercuric oxide floated on the surface of mercury in an inverted vessel, the open mouth of which was immersed in mercury in a dish. The rays of the sun, focussed on the red powder by a lens, formed the source of heat.

A gas was liberated which drove down the level of the mercury in the vessel. Priestley was surprised to find that a candle burned better in the gas than in air, that mice placed in it suffered no injury, and that it could be taken into his own lungs without pain. During a visit to Paris he informed Lavoisier of the discovery, whereupon the latter carried out the experiment upon the heating of mercury in air which has already been described. It was Lavoisier who named the gas "oxygen," and it was also he who explained the indispensable part played by it in the burning of combustible substances, in the conversion of metals into their oxides, and in respiration.

25. Preparation from mercuric oxide. The apparatus used at present in obtaining oxygen from mercuric oxide is shown in

Figure 17. The vessel in which the mercuric oxide is heated is called a *retort*. It is connected with a bulb, which receives the mercury. The oxygen passes on and is collected over water. This is a most instructive experiment, but mercuric oxide is too expensive for use in preparing oxygen in any large quantity. For this purpose much cheaper materials are available.

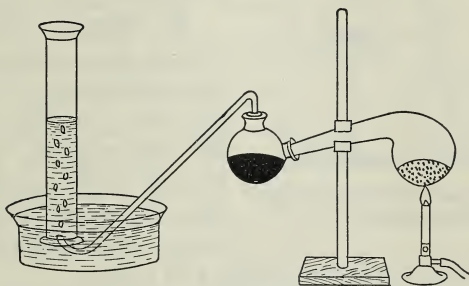


Fig. 17. Preparation of oxygen from mercuric oxide.

26. Preparation from potassium chlorate. One of the most convenient is *potassium chlorate*, a white powder which contains nearly two-fifths of its weight of oxygen (39.18 per cent). It also contains *potassium* and *chlorine*, two important elements which will be studied later. When potassium chlorate is heated, oxygen is given off, and a white mass called *potassium chloride*, composed of potassium and chlorine, remains.

In the actual preparation the potassium chlorate is mixed with about half its weight of a black powder called *manganese dioxide*. This causes the oxygen to escape at a lower temperature and with less danger of explosion than when potassium chlorate is heated alone. The manganese dioxide remains unchanged after the experiment, mixed with the potassium chloride. Thus the manganese dioxide, without being affected itself, controls the decomposition of the potassium chlorate. The term **catalytic action**, **contact action**, or **catalysis** is applied to behavior of this sort.

The apparatus is shown in Figure 18. The mixture of potassium chlorate and manganese dioxide is heated in a *flask*, which is protected from the flame by wire gauze to prevent cracking of the glass by excessive heat. The oxygen is collected over water.

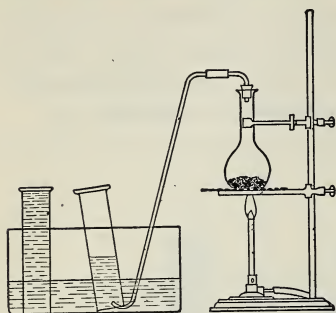


Fig. 18. Preparation of oxygen from potassium chlorate.

27. Physical properties.

Oxygen is a colorless, odorless, tasteless gas. It is heavier than air. A liter of air at the temperature of melting ice and under a pressure of one atmosphere weighs 1.293 grams, while a liter of oxygen,

under the same conditions weighs 1.43 grams.

By the combined application of pressure and extreme cold, oxygen can be condensed into a light-blue, magnetic liquid, which, under atmospheric pressure, boils at -182°C . Upon further cooling to -235°C ., liquid oxygen freezes to a pale-blue solid.

The solubility of oxygen in water is small: 100 cubic centimeters of water at room temperature (20°C .) dissolve only 3 cubic centimeters of the gas. Even this slight solubility, however, is of great importance, since without it aquatic life would be impossible.

28. Chemical conduct. A simple method of ascertaining how oxygen behaves with other substances is shown in Figure 19. The substance is placed in the bowl of an iron spoon, heated until it begins to burn, and plunged into a bottle of the gas. In this way it can be shown that powdered zinc and iron burn brightly in oxygen, and that the products are the same as those obtained by heating the same metals in the air, that is,



Fig. 19. Burning metals in oxygen.

zinc oxide and *iron oxide*. Hence, if the air were pure oxygen, the use of iron grates and stoves would be impossible, since the metal would burn as readily as the fuel.

Energetic chemical combination accompanied by the production of light and heat is called **combustion**. The conduct of oxygen can be summed up in the statement that in the cold its action upon most other elements is slight, but at high temperatures it becomes active and combines with many other elements with combustion. The combination is more violent in oxygen than in air because each liter of pure oxygen contains about 5 times as much oxygen by weight as a liter of air. A liter of air contains only 0.3 gram of oxygen, while a liter of oxygen contains 1.43 grams. Substances burn more rapidly in oxygen than in air, therefore, because oxygen is supplied to them 5 times as liberally. For this reason a wooden splint bearing a spark bursts into flame when introduced into oxygen. This "spark test," as it is called, is a convenient method of detecting the gas.

Sulphur, heated in a spoon, burns slowly in air, but in oxygen the combustion becomes energetic. The product is *sulphur dioxide*, a colorless gas with a sharp, suffocating odor.

Phosphorus and **magnesium** burn in oxygen with a brilliancy which the eye can scarcely bear, and with the production of such a high temperature that the bottle is often broken in the experiment. In fact, the experiment of burning phosphorus in oxygen is sometimes fancifully called the "chemical sun." The oxides of both phosphorus and magnesium are white powders.

Charcoal heated in the air and plunged into oxygen burns rapidly to a colorless gas called *carbon dioxide*. If we went through the list of the elements, trying the behavior of each of them with oxygen, we should find a few, like gold, platinum, and some others, on which it has no action, but most of them would unite with it, either rapidly with combustion, or slowly. Oxygen, then, especially at high temperatures, is a very **active** element.

29. Flame. Sulphur burns in oxygen with a large, pale flame; iron burning in oxygen gives a brighter light and a higher temperature, but no flame is seen. The cause of this difference is that the sulphur is more easily converted into vapor than is the iron. The sulphur is vaporized by the heat of its own combustion, and the surrounding space becomes filled with a hot mixture of sulphur vapor, oxygen, and sulphur dioxide, which becomes *incandescent* and appears as flame. Iron is not vaporized at all by the heat produced when it combines with oxygen. The oxygen must go to the iron, which glows brightly, but since the chemical change does not extend into the surrounding space, there is no flame.

A combustible gas, like hydrogen or illuminating gas, will, of course, burn with a flame. Candles, oil, paper, and wood yield a flame because they are converted wholly or partly into gases before combination with oxygen occurs.

30. The Bunsen burner. Illuminating gas burns with a bright, yellow flame, which at once deposits soot on any object placed in it. If air is mixed with the gas before it is burned, the presence of the extra oxygen produces a striking change in the flame, which becomes blue, non-luminous, and free from soot, and acquires a higher temperature.

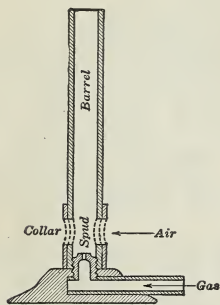


Fig. 20. The Bunsen burner.

The *Bunsen burner* is a device for automatically mixing the gas, before it reaches the flame, with the proper quantity of air. A diagram of the burner is shown in Figure 20. The gas, escaping from the "spud," as it rushes up the chimney produces a partial vacuum which continuously draws in air through the holes in the collar. By turning the collar the volume of air mixed with the

gas can be regulated. In the laboratory it is frequently necessary to turn the flame down, since for many purposes a small

flame is better than a large one. Whenever this is done, the size of the holes should be reduced; otherwise the flame will "strike back" and burn inside the chimney at the top of the spud. A burner that has "struck back" should be extinguished at once, for it becomes intensely heated and may be a source of serious danger. The rubber supply tube, for instance, might be melted by the hot burner. Were the damaged rubber tube and the gas issuing from it to become ignited, the risk of a serious fire would be very grave. Moreover, a burner that has "struck back" gives off gases which have an offensive odor and are quite poisonous.

31. The Bunsen principle in the household. The principle of the Bunsen burner is applied in all heating, cooking, and lighting with gas. The burners of the gas range are merely

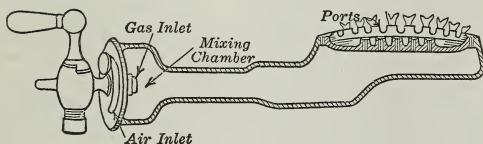


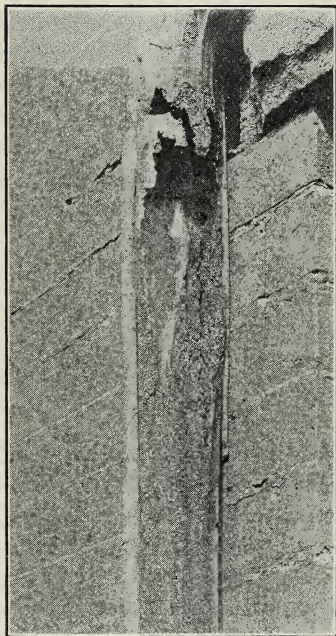
Fig. 21. The Bunsen principle in the burner of the gas range.

Bunsens which, instead of one large flame, produce many small ones, while the Welsbach light is simply a Bunsen flame with a gauze mantle supported in it as a source of light.

The volume of air supplied to the burners of the gas range can be regulated by means of a small slide at the base of the burner, which answers the same purpose as the collar of the laboratory burner. This slide should be so adjusted that the blue-green cone in the centre of the flame is about half the height of the whole flame. The flame should be *silent*. If it is short, makes a roaring noise, and is inclined to strike back, too much air is being admitted, whereas a long, partly yellow flame with a tendency to deposit soot is an indication of insufficient air supply. A pungent odor from a gas stove or lamp of any kind is a sign of danger, for it indicates incom-

plete combustion, which means that a highly poisonous gas (*carbon monoxide*) is escaping. A gas stove should be connected with a chimney so that the combustion products may be carried off and not discharged into the air of the room.

32. Slow oxidation. The process of combination with oxygen is called **oxidation**. The **rusting** of metal shows that oxidation occurs, not only at high temperatures, but also, though much less rapidly, in the cold. This slow oxidation of iron causes annual losses of millions of dollars and necessitates large expenditures for paint and other protective coatings, which are applied to ironwork to prevent rusting.



Courtesy of the New Jersey Zinc Co.

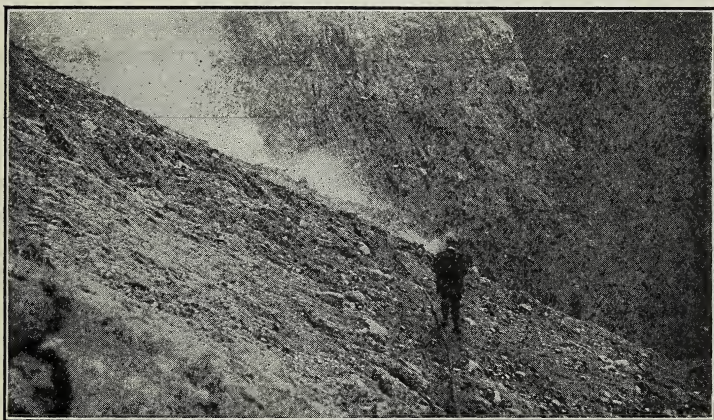
Fig. 22. An iron pipe destroyed by rusting or slow oxidation.

Coal also oxidizes slowly at ordinary temperatures, though the product is not a rust, but a colorless gas, which is called *carbon dioxide* because it is a compound of carbon and oxygen. This slow combustion of coal, especially soft coal, becomes an important practical matter where thousands of tons are stored. The combination of carbon with oxygen generates much heat, and it often happens that a tem-

perature is produced high enough to set fire to the coal.

Slow oxidation that develops into actual burning in this way is often called **spontaneous combustion**. It may also occur in oily rags which have been used to wipe machinery or which

have been discarded by painters. Spontaneous combustion is to be feared only in oils of vegetable or animal origin. Linseed, menhaden, corn, cottonseed, neatsfoot, and lard oils are subject to it, the danger decreasing in the order named. Rags or waste saturated with vegetable or animal oils should be promptly burned after use. Mineral oils are not subject to spontaneous combustion, and when mineral oils are mixed with animal or vegetable oils, the risk of it is slight.



Courtesy of Bureau of Mines,

Fig. 23. Fire caused by spontaneous combustion in a slate containing carbon and sulphur.

33. Effect of rising temperature. The fact that coal oxidizes slowly at ordinary temperatures is well known to miners. In this way the air of coal mines is constantly being robbed of its oxygen, and unless the ventilation of the mine is good, the atmosphere becomes suffocating and dangerous.

Oxidation is very slow in the mine, but is very rapid in the furnace, because the temperature of the latter is higher by about $1,000^{\circ}\text{C}$. As a general rule, a rise in temperature of 10°C . doubles the speed of a chemical change. This is one

reason for the frequent use of heat in the laboratory and in the chemical works: it quickens processes and saves time. Take, for example, the case of coal:

- A rise of 10° multiplies the speed by 2
- A rise of 20° multiplies the speed by 2×2 , or 2^2
- A rise of 30° multiplies the speed by $2 \times 2 \times 2$, or 2^3
- A rise of $1,000^{\circ}$ multiplies the speed by 2^{100}

2^{100} is about equal to the number 126 followed by 28 ciphers. Hence the cause of the striking difference in the behavior of



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Fig. 24. United States destroyers laying an impenetrable smoke screen produced by cutting down the air supply to oil-burning boiler furnaces.

coal at ordinary temperatures and when heated becomes clear. It forms a perfect illustration of the accelerating effect of rising temperature upon chemical change.

The object of the *chimney* is to insure a continuous and adequate supply of air to the burning coal. The gas in the chimney, being heated, expands, becomes light, rises, and escapes at the top of the stack. This draws in air at the bottom, through the grate, to the fuel bed. The higher the chimney, the greater the *draft* caused by the rising gases. The furnace is controlled by limiting the volume of air admitted and thus the amount of oxygen available for combustion.

Smoke, which consists of minute particles of unburned carbon, results from insufficient air supply for complete combustion.

34. Kindling temperature. When coal is heated, as we have seen, the slow oxidation becomes more and more rapid. In the same ratio the heat *produced*, independently of the outside heating, increases. At first this heat is dissipated, but as the speed of the oxidation increases with the rising temperature, more heat is generated than can be removed by radiation and conduction, so that the coal itself heats up rapidly and finally "takes fire." The stage at which combustion appears is called the **kindling temperature**. When this point has been reached, combustion becomes self-supporting without external heat, provided that abundant supplies of coal and of oxygen are present.

The kindling temperature varies greatly in different substances. The diamond must be heated to whiteness before it will burn, but phosphorus ignites from the warmth of the hand, so that it is dangerous to touch. A powder usually has a much lower kindling temperature than a compact mass of the same substance. A bar of iron can be melted in the air before the kindling temperature is reached, but the kindling temperature of finely powdered iron lies below the ordinary temperature of a room, so that when a tube containing the powder is opened without heating and the metal shaken out, a shower of sparks is produced.

A sudden blast of cold air may extinguish a small flame by cooling the burning substance below the kindling temperature, but if the flame is large, the cooling effect is slight, and the vigor of the combustion is increased by the additional supply of oxygen. Thus the same procedure that puts out a match or a candle increases the energy of a log fire. The quenching effect of "stamping out" a blaze, or of covering it with a rug, depends upon the exclusion of air, without which combustion must cease even though the burning substance may be far above the kindling temperature.

35. Oxygen and life. Free oxygen is essential to life. When it is withdrawn, the more highly organized the animal, the more quickly death results. The tissues of the body are continually oxidizing, and this slow combustion is the source of the energy that manifests itself in the body as heat and as work. The automatic control of this oxidation, which keeps the temperature of the body almost constant at 37°C ., is one of the most marvellous facts of physiology. The oxygen is carried about the body by the blood, which in a healthy adult contains about a liter of oxygen. This oxygen supply is constantly being consumed in oxidizing the tissues and constantly being replenished through the lungs. A greater weight of oxygen than of food is required by the human body each day.

Thus the body, like an engine, requires fuel, and this fuel is the *food*, which consists of complex substances rather poor in oxygen and capable of slow oxidation with liberation of heat. The energy that a food can yield to the body can be ascertained precisely as we estimate the energy in a sample of coal, that is, by burning a fixed weight of it and measuring the amount of heat produced.

36. Effect of air poor in oxygen. We have seen that, because of the slow oxidation of coal, air containing much less than the normal 21 per cent by volume of oxygen is often met with in coal mines. The effect of inhaling such an atmosphere is as follows, the percentages of oxygen being by volume:

- 17 per cent.—Miner's oil lamp extinguished; respiration normal.
- 12 " —Miner's acetylene lamp extinguished; respiration deeper than normal.
- 10 " —Slight panting.
- 5 " —Marked panting and mental confusion; probably fatal in time.
- 2 " —Loss of consciousness without warning in less than a minute. So long as the heart beats (10 minutes or more) life can be restored by artificial respiration, which may have to be kept up for a long time.

37. Source of the free oxygen of the air. The cycle through which oxygen passes in nature can be represented as in Figure 25. This diagram means that the oxygen of the air is taken up by animals, who give off a liter of carbon dioxide for each liter of oxygen they consume. This carbon dioxide is decomposed by the plants, which build up the carbon into their tissues and return the oxygen to the air, whereupon the cycle begins anew. An acre of forest discharges daily about a ton of oxygen.

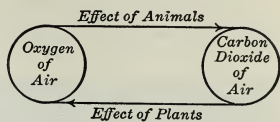


Fig. 25. The cycle of oxygen in nature.

It is probable that the plants annually restore to the atmosphere just about as much oxygen as the animals (including man) remove from it by respiration and combustion. Fairly exact analyses of the air have been made for nearly a century, but they have not shown any change in the percentage of oxygen. Air that had been sealed up in vases in the ruins of Pompeii for almost two thousand years proved to contain the same proportion of oxygen as the present atmosphere.

38. Oxygen in industry. The chief industrial use of oxygen is in connection with the production of high temperatures. Flames of hydrogen and of other gases, fed with oxygen, are produced by means of a special burner called the **oxy-hydrogen blowpipe**, the construction of which will be clear from Figure

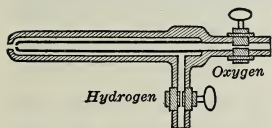


Fig. 26. Principle of the oxy-hydrogen blowpipe.

26. It consists of an inner tube conveying the oxygen under pressure, surrounded by a larger tube which carries the hydrogen or other combustible gas, also under pressure. A cylinder made of lime, or of some other solid that will resist the temperature, glows brightly when heated in such a flame, giving what is called the **lime light**, which is employed for projecting motion and stereopticon pictures where electric light is not

available. For this purpose illuminating gas, compressed in steel cylinders, is used with the oxygen.

Far more important than the lime light is the use of such high-temperature flames in working metals. A 6-in. shaft of



Courtesy of the Air Reduction Sales Co.

Fig. 27. Welding an iron flag pole with the oxy-acetylene blowpipe.

solid steel has been cut through with a burner of this type in 40 seconds; in another test, a circle 20 in. in diameter was cut out of 1-in. steel plate in 45 seconds. Welding of metals and local repairs on machinery are further important applications. The hottest of flames is that of *acetylene* fed with oxygen, which is largely employed for the purposes just mentioned. Its temperature is nearly 4,000° C.

Oxygen, compressed in steel cylinders, is always at hand in hos-

pitals for use in cases of incipient suffocation due to pneumonia and other causes. It is employed, in an instrument called the "pulmotor," in the resuscitation of cases of insensibility resulting from partial drowning or from the inhalation of illuminating gas. Miners who volunteer on rescue parties after mine fires or accidents often carry respiratory apparatus fed from a cylinder of oxygen, for they may be obliged to pass through gases that would be fatal without protection of this kind. Aviators who ascend to great heights must carry

similar breathing apparatus to supply the deficiency of oxygen in the rarefied air at high altitudes.

For these industrial purposes oxygen is made at present by two methods only, (1) from air, by partial liquefaction, and (2) from water, by decomposition by the electric current. Air



Courtesy of the Bureau of Mines.

Fig. 28. A mine rescue crew equipped with oxygen breathing apparatus.

and water are materials that may be had without expense, which is a decisive consideration from the industrial point of view. Both these methods of obtaining oxygen will be fully discussed later.

OZONE

39. A modification of oxygen. When electric waves are passed through oxygen, energy is absorbed and a second modification of the element, called **ozone**, is produced. The apparatus employed on the lecture table for obtaining small quantities of ozone is shown in Figure 29. The double-walled tube is

coated inside and out with tin foil. The outside coating is connected with one pole of an induction coil, and the inside coating with the other. The electric discharges between the two coatings pass through the oxygen, which enters and leaves the tube as shown by the arrows. Only about 10 per cent of

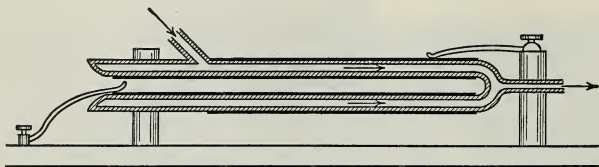


Fig. 29. Apparatus for generating ozone.

the oxygen can be converted into ozone by this apparatus. Lightning flashes produce traces of ozone in the air, and its odor can sometimes be detected during thunder-storms.

40. Physical properties. Pure ozone is a blue gas, which, by intense cooling, can be condensed to a blue-black, explosive liquid. It has a peculiar odor, and in any considerable quantity it is irritating to the respiratory organs and poisonous. Ozone gas is $1\frac{1}{2}$ times as dense as oxygen; hence, if 3 liters of oxygen were entirely changed to ozone, 2 liters of ozone would be produced. When passed through a warm glass tube, ozone reverts completely into oxygen; from every 2 liters of ozone present, 3 liters of oxygen are produced.

41. Chemical conduct. When oxygen is changed into ozone, energy is absorbed from the electric waves. Hence, ozone contains more energy than oxygen, and is far more active, especially at ordinary temperatures. Oxygen in the cold has no effect on silver or mercury, but ozone rapidly converts both metals into oxides. Rubber tubing must be avoided in working with ozone, as it acts rapidly on the rubber. It bleaches dyes, decolorizes blood, and attacks plant and animal matter.

42. Uses. Ozone is used in industry in bleaching and deodorizing oils, fats, tallow, and waxes. It is employed as an

adjunct to ventilation, especially to remove odors, in such places as tanneries, slaughter-houses, and fertilizer plants, and in overcrowded rooms. The use of ozone for disinfecting the air of hospitals, halls, and theaters is unwise, as it has little action upon the bacteria of the air and is irritating to the lungs. Ozone, however, is an efficient disinfectant for *water*. For this purpose air is charged with ozone by passing it through an apparatus similar in principle to that shown in Figure 29. This ozonized air enters at the bottom of a tall tower, to which the water, previously filtered, is admitted at the top. Perforated plates at intervals in the tower divide the ozonized air into numerous small bubbles to secure intimate contact between the ozone and the water. The water, flowing from the bottom of the tower, is found to be almost completely sterilized. The municipal water supplies of Paris, Petrograd, Lille, and many other European cities are treated by this method.

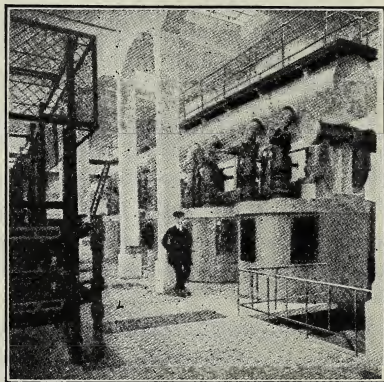


Fig. 30. Ozone batteries and sterilization towers in the Petrograd water works.

SUMMARY

Oxygen is the most abundant of the elements.

On a small scale it may be prepared by heating a mixture of **potassium chlorate** with **manganese dioxide**. The manganese dioxide remains unaltered after the experiment, yet, when it is present, the oxygen escapes more readily from the potassium chlorate. The term **catalytic action**, or **catalysis**, is applied to effects of this kind, which are very numerous.

Catalytic action occurs in all instances in which chemical

changes are facilitated by the presence of substances that are themselves unaffected by the change.

Catalytic action is often called **contact action**.

Oxygen is slightly soluble in water: were it not for this fact, aquatic life would be impossible.

In the cold the union of oxygen with other elements is slow, as in the rusting of metals. At higher temperatures combination becomes more and more rapid. The temperature at which *combustion* appears is the **kindling temperature**.

A gas, or a substance that is converted into a gas by the heat of its own combustion, will burn with a **flame**. A substance that produces no gas during combustion will merely **glow**.

When air is mixed with illuminating gas before the gas is burned, the flame becomes blue, acquires a higher temperature, and does not deposit soot. Practically all gas is now burned in this way.

Slow oxidation that finally heats the substance sufficiently to cause it to burst into flame is called **spontaneous combustion**. It may occur in coal or in rags wet with oils of vegetable or animal origin.

The heat developed in the bodies of animals is due to the slow oxidation of materials supplied by the food. The product of this oxidation is *carbon dioxide*, which is exhaled into the air.

Mine air that extinguishes a flame may contain sufficient oxygen to support respiration.

The free oxygen of the air comes from the plants, which decompose carbon dioxide and return the oxygen to the atmosphere.

On a large scale oxygen is made only from water or from air.

Ozone, though it contains nothing but oxygen, is quite different from ordinary oxygen, and much more active. It is made by passing electric discharges through oxygen or air.

Oxygen and ozone are said to be **allotropic forms** of oxygen; this term is applied to all cases in which the same element exists in different modifications.

EXERCISES

1. Explain the shares of Priestley and of Lavoisier in the discovery of oxygen, in its extraction from air, and in the explanation of the part played by it in nature.
2. Define *catalytic action* and give an instance.
3. What is the volume in liters of 2.86 grams of oxygen?
4. What is the weight in grams of 22.4 liters of oxygen?
5. How many grams of oxygen can be obtained by heating 5 grams of potassium chlorate with manganese dioxide? How many liters? Why is it unnecessary to know the weight of the manganese dioxide in order to solve this problem?
6. What special importance attaches to the fact that oxygen is somewhat soluble in water?
7. What is *flame*? Under what conditions is combustion flameless?
8. Examine the home gas range and the Welsbach light, and explain how the Bunsen principle is applied in both cases.
9. What two classes of oils are liable to spontaneous combustion? Mention three oils that are dangerous in this respect.
10. What is meant by the *kindling temperature*? What is the effect of fine subdivision upon it?
11. In making a coal fire what is the purpose of the paper? The wood? Why does the same wood burn more readily in shavings than in the form of a compact log?
12. Explain the action of a cold blast of air (*a*) upon a candle flame, (*b*) upon a log fire.
13. Give two reasons why water extinguishes fire.
14. Why is it suicidal for a person whose clothing has caught fire to run about?
15. Explain the good effect of wrapping a rug around the victim of such an accident.
16. How is the temperature of the body maintained constant?
17. Oxygen is a very active gas and is continually entering into chemical combination with various materials, yet the percentage of free oxygen in the air remains the same from year to year. Why?

18. Over a billion tons of coal are burned each year and each ton yields about three tons of carbon dioxide, but the percentage of carbon dioxide in the air has shown no increase in half a century. Why?

19. What is the cycle through which oxygen passes in nature?

20. What are the chief uses of oxygen? How is it made on a large scale?

21. How is ozone obtained? Explain its use in sterilizing water.

22. What is *allotropy*? Give examples.

23. If 75 c.c. of oxygen could be changed completely to ozone, how many cubic centimeters of ozone would be obtained?

24. 115 c.c. of oxygen were partly converted into ozone. The volume contracted to 110 c.c. When the gas was gently heated the original volume was exactly restored. Calculate (a) the number of cubic centimeters of ozone which had been produced, and (b) its percentage by volume.

25. 160 c.c. of oxygen containing ozone were heated. The volume became 170 c.c. (a) How many cubic centimeters of ozone and (b) what percentage of it by volume were present?

REVIEW QUESTIONS

1. Students in reciting often state that mercury and oxygen *mix* to form mercuric oxide. Correct the error.

2. The evidence that ozone is a form of oxygen is as strong as the evidence that ice is a form of water. Explain what is meant by this statement.

CHAPTER V

GASES AND THEIR MEASUREMENT

43. Effect of pressure on the volume of gases. In 1660 the famous Robert Boyle investigated the loss in volume produced in a confined mass of air by increasing the pressure under which the gas is confined. The apparatus used by Boyle, which is still employed in the physical laboratory, is shown in Figure 31.

The air is contained in the short closed limb of the tube, and mercury is poured into the open limb until the columns of mercury in the two limbs are of the same height. The column of air is then measured; the pressure upon it, of course, is that of the atmosphere.

Now the pressure of the atmosphere is equal to that of a column of mercury 760 mm. (approximately 30 in.) high. Hence, if we pour mercury into the open limb until it stands 760 mm. above its level in the closed limb, the pressure on the air is doubled, becoming 2 atmospheres instead of 1. When the air is again measured, under the double pressure, its volume is found to be exactly halved. If the open limb of the tube is long enough, we can proceed, in the same way, to measure the air under a pressure of 3 atmospheres, when it will be found to occupy one-third its original volume.

The greater the pressure, then, the smaller the volume; doubling the pressure squeezes the air into half the original volume; tripling the pressure reduces it to one-third the original volume; and so on. Gases other than air behave in exactly



Fig. 31.—Boyle's apparatus.

the same way. This fact is called **Boyle's Law**. It may be stated as follows:

The volume of a mass of gas varies inversely as the pressure upon it.

Let P_1 = the initial pressure, P_2 the final pressure, and V_1 and V_2 the corresponding volumes. Then:

$$V_1 : V_2 :: P_2 : P_1$$

$$V_2 = V_1 \times \frac{P_1}{P_2}$$

The final volume is obtained by multiplying the initial volume by the initial pressure and dividing by the final pressure.

For example: 4 liters of air are measured under a pressure of 2 atmospheres. What will the volume become at 4 atmospheres?

Here the initial pressure is 2 atmospheres, and the final pressure is 4 atmospheres. Hence we have:

$$\text{Final volume} = 4 \times \frac{2}{4} = 2 \text{ liters}$$

Pressures are usually measured by the height of the mercury column in the barometer, and are therefore stated in *millimeters*.

For example: 8 liters of oxygen were measured under a pressure of 760 mm. To what volume will the gas expand when the pressure is reduced to 380 mm.?

Here 760 is the initial pressure and 380 the final pressure. Hence:

$$\text{Final volume} = 8 \times \frac{760}{380} = 16 \text{ liters}$$

44. Absolute temperature. For reasons which lie outside the scope of this book, it is universally believed that if a body were robbed of all heat, its temperature would be 273°C . below the melting point of ice, which forms the *zero* of the centigrade scale. This temperature, -273°C ., which denotes the total absence of all heat, is called the **absolute zero**. Temperatures within about 1 degree of the absolute zero have

been obtained in the laboratory. The temperature measured from the absolute zero upward is termed the **absolute temperature**. Thus, the temperature of melting ice, which is 0°C. , is 273° absolute, while that of boiling water, 100°C. , is 373° absolute.

A properly heated room has a temperature of 20°C. , which is 293° absolute.

Let T = the absolute temperature and t the centigrade temperature; then,

$$T = t + 273$$

45. Effect of temperature on the volume of gases. In 1802 the French physicist *Charles* measured the expansion produced in a measured volume of air when warmed through a definite number of degrees centigrade. He extended his investigation to other gases, and found that they all expanded to the same extent for the same rise in temperature. The outcome of his work was the following law, which is known as **Charles' Law**:

The volume of a mass of gas is proportional to its absolute temperature.

Let T_1 and T_2 equal the initial and final absolute temperatures, and V_1 and V_2 the corresponding volumes. Then:

$$V_1 : V_2 :: T_1 : T_2$$

$$V_2 = V_1 \times \frac{T_2}{T_1}$$

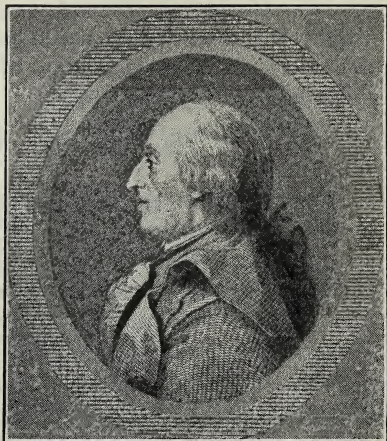


FIG. 32. JACQUES ALEXANDRE CÉSAR CHARLES (1746–1823).

French physicist; discovered the relation between temperature and volume in gases expressed in what is known as Charles' Law; substituted hydrogen for heated air in balloons and in 1783 made the first balloon ascension.

The final volume is obtained by multiplying the initial volume by the final absolute temperature and dividing by the initial absolute temperature.

For example: a liter of oxygen was measured at 0°C . What will the volume become at 273°C ?

First it is necessary to change both temperatures to the absolute scale. The absolute temperature of 0°C . is 273° , while 273°C . is 546° absolute. Then we have:

$$\text{Final volume} = 1 \times \frac{546}{273} = 2 \text{ liters}$$

The student will find it necessary to be on his guard against the tendency to use the ordinary centigrade temperatures in the calculation. Thus, in the preceding problem, if we neglect the change of the temperatures to absolute, we have:

$$\text{Final volume} = 1 \times \frac{273}{0}$$

That is, the final volume is infinite, which is impossible.

46. Combined effect of temperature and pressure. When temperature and pressure both change, the final volume can nevertheless be obtained in one calculation, for the effects of temperature and pressure upon the volume are independent of each other. We have:

$$\text{Final volume} = \text{Initial volume} \times \frac{\text{Final abs. temp.}}{\text{Initial abs. temp.}} \times \frac{\text{Initial pressure}}{\text{Final pressure}}$$

Or, using the symbols with the same meaning as before:

$$V_2 = V_1 \times \frac{T_2}{T_1} \times \frac{P_1}{P_2}$$

If t_1 and t_2 are the initial and final centigrade temperatures, the equation becomes:

$$V_2 = V_1 \times \frac{273+t_2}{273+t_1} \times \frac{P_1}{P_2}$$

Consider, for example, the following problem: 100 c.c. of

oxygen, measured at 15° C. and at 740 mm., will occupy what volume at 0° C. and 760 mm.?

Here the initial absolute temperature is 288, and the final, 273. Since the oxygen is to be cooled, it will contract. Hence the fraction for calculating the change in volume due to temperature is $\frac{273}{288}$.

The initial pressure is 740, and the final, 760. Since the pressure on the oxygen is to be increased, this also will produce contraction. Hence the pressure fraction must be $\frac{740}{760}$. Therefore we have:

$$\text{Final volume} = 100 \times \frac{273}{288} \times \frac{740}{760} = 92.3 \text{ c.c.}$$

47. Standard conditions. Since the volume of a mass of gas varies according to the conditions under which it is measured, an expression like "100 c.c. of oxygen" has no definite meaning unless some temperature and pressure are either stated or understood. In order to avoid this difficulty, it is convenient to agree upon some temperature and pressure as *standard conditions*, to be understood when no statement about the conditions under which the gas was measured is made. *Zero centigrade* is chosen for the **standard temperature**, because it can easily be obtained in the laboratory by surrounding the vessel containing the gas with melting ice. For the **standard pressure**, 760 mm. of mercury, which is about the average pressure of the air, is adopted. It amounts to a little more than a kilogram per square centimeter, or about 15 lb. per square inch. The standard pressure is often called the *pressure of 1 atmosphere*.

Hence, when a writer refers simply to "100 c.c. of oxygen," it is understood that 0° C. and 760 mm. are the conditions of measurement.

In practical work it frequently happens that a gas is measured at room temperature and under the pressure shown by the barometer at the time, and it is necessary to calculate the

volume under *standard* conditions. Here the final temperature is 273° absolute, and the final pressure 760 mm. Hence,

$$V_2 = V_1 \times \frac{273}{T_1} \times \frac{P_1}{760}$$

$$\text{Final volume} = \text{Initial volume} \times \frac{273}{\text{Initial abs. temp.}} \times \frac{\text{Initial pressure}}{760}$$

48. Balloons. From Boyle's Law it follows that a balloon completely filled and sealed at the surface of the earth would burst when it ascended, since as the atmospheric pressure grew less, the gas would expand, and the frail envelope would ultimately be unable to withstand it. Either the filling of balloons must be only partial, or a valve must be provided through which the gas can escape as the external pressure decreases. The student will perceive that the expansion on rising and the contraction on descending bring about a wastage of gas and a decrease in lifting power, which, unless there is some special mechanism for preventing the wastage, will finally bring an airship to the ground.

49. The gas meter. The standard cubic foot of illuminating gas is supposed to pass through the meter at 60° F., which is about 15° C. Frequently the meter is placed close to the furnace, and the average temperature at which the gas is measured is 70° F. or over. Since the absolute zero is -460° F., this entails an increase of $\frac{10}{460}$, or $\frac{1}{46}$, in the apparent volume of gas passed, which raises the gas bills by about 2.2 per cent.

The elevation above sea level of Denver, Colorado, is 1 mile, and that of Leadville, Colorado, nearly 2 miles. In such localities the expansion of illuminating gas due to reduced pressure, according to the law of Boyle, becomes quite important, and unless there is some concession in the rate at which the gas is sold, a serious injustice to the consumer results. In fairness, however, it should be added that the tendency of most meters is to register too low, rather than too high, and that, as a rule, there is little reason for complaints against their accuracy.

50. The diffusion of gases. In Figure 33 C_1 and C_2 are two cylinders of the same size, ground to fit air-tight. The upper cylinder is filled with nitrogen and the lower with oxygen. Nitrogen is decidedly lighter than oxygen; nevertheless, the two gases mix, and in a little while we find in all parts of both cylinders a mixture containing half its volume of each gas. Other pairs of gases act in the same way. Each gas travels into the other until there is a uniform mixture. This is called the **diffusion of gases**. The term means that actual motion of both gases from one part of the apparatus to another has occurred. It takes place even when the cylinders are left entirely at rest, and when change of temperature is excluded.

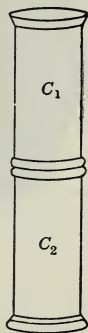
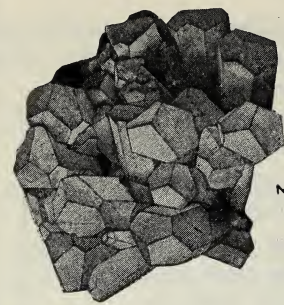


Fig. 33. Diffusion of gases.

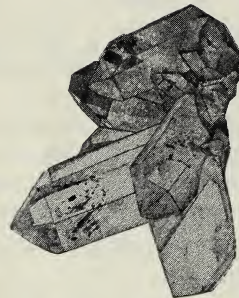
51. Comparison of solids, liquids, and gases. No general laws corresponding to those of Boyle and of Charles have been discovered for solids and liquids. When warmed or compressed, each solid and each liquid expands or contracts *in its own way*, and the change in volume can be determined only by experimenting with the substance in question.

In equal volumes solids and liquids are very much heavier than gases. Water is about 800 times as dense as air, and lead more than 8,000 times as dense as oxygen. The heaviest of solids (a metal called *osmium*) is 250,000 times as dense as the lightest of gases, hydrogen.

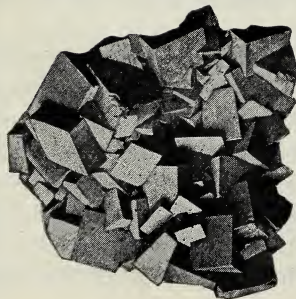
Liquids and gases *take the shape of the containing vessel*, while a solid has a *form of its own*, which it retains until it is changed by external force. Many solids occur in nature in specific forms. Thus, the minerals are usually found in **crystals**, the form of which, in each case, is characteristic, and furnishes one of the most important means of identifying the mineral. *Crystals are bounded by plane surfaces, which meet in sharp edges.* The crystalline form is due wholly to the internal



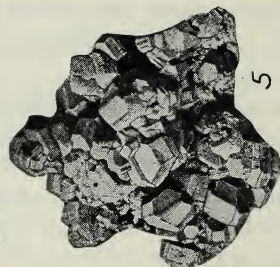
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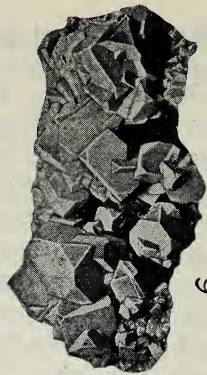
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6

tendency of the substance to arrange itself in that particular way, and not to external action of any kind.

If we pour half a liter of water into a liter bottle, the water remains in the bottom, and its upper boundary is distinct. A liquid in a vessel that it only partially fills possesses a limiting upper surface, but a gas, as we have seen, distributes itself evenly throughout any vessel to which it is admitted. Half a liter of gas, allowed to enter an empty liter bottle from which all the air has been removed by an air pump, will fill the bottle completely. The pressure of the gas, as we can see from Boyle's Law, will sink to one-half its original value.

MEASUREMENT OF GASES IN THE SCHOOL LABORATORY

52. Measurement of gases over water. In the school laboratory gases are always measured over *water*. Before the measurement is made, it is usual to make the level of the water inside and outside the measuring vessel the same (Fig. 35A); if this is not done, the pressure under which the gas is measured will be either less or greater than that of the atmosphere at the time of measurement. If the level of the water inside the measuring tube were *above* that of the water outside (B), the actual pressure on the gas would be *less* than that of the atmosphere, while if the surface of the water inside the measuring tube were *below* that of the liquid outside (C), the gas would be measured under a pressure *greater* than that of the atmosphere as indicated by the barometer in the laboratory.

In most cases the levels can be equalized by raising or lowering the measuring tube. Sometimes, however, this

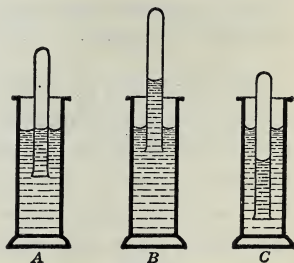


Fig. 35. Measurement of gases over water.

adjustment of the apparatus is impossible (Fig. 36). In such circumstances the difference between the levels can be measured in millimeters with a meter stick.

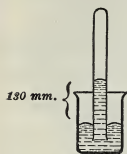


Fig. 36.

Since mercury is approximately 13 times as dense as water, the difference of level in millimeters must be divided by 13 to convert it into millimeters of mercury. The quotient is *subtracted* from the barometer reading if the level of the water in the measuring tube is *above* that in the outer vessel (Fig. 36). If the difference of levels were in the other direction, the quotient would be *added* to the barometer reading, but in an actual case of this kind the measuring tube can always be raised until the levels inside and outside are the same.

For example, suppose that in Figure 36 the distance from the surface of the water in the graduated tube to the surface of the water in the cylinder is 130 mm. Dividing 130 by 13 we find the length of the equivalent column of mercury to be 10 mm. If the barometer in the laboratory gave a reading of 759 mm. at the time, the actual pressure on the gas becomes $759 - 10$, or 749 mm.

The pressure of water vapor. When a gas is measured over water, water evaporates and mixes with the gas, so that a portion of the total pressure is supported, not by the gas being measured, but by the **water vapor** that is mixed with it. *The true pressure under which the gas is measured is obtained by subtracting from the observed pressure the pressure due to the water vapor that escapes from liquid water at the temperature of measurement.*

The pressure of water vapor depends upon the temperature, increasing as the temperature rises. The pressures of water vapor have been carefully determined for all important temperatures, and are given in the following table. When a gas has been measured over water, the pressure of water vapor for the temperature at the time of measurement, obtained from the table, should be subtracted from the barometric pressure at the

time. The remainder is taken in the calculation as the *original pressure*.

PRESSURE OF WATER VAPOR

Temperature, Centigrade	Pressure in Millimeters of Mercury	Temperature, Centigrade	Pressure in Millimeters of Mercury
10°	9.2	21°	18.5
11°	9.8	22°	19.7
12°	10.5	23°	20.9
13°	11.2	24°	22.1
14°	11.9	25°	23.5
15°	12.7	26°	25.0
16°	13.5	27°	26.5
17°	14.4	28°	28.1
18°	15.4	29°	29.8
19°	16.4	30°	31.6
20°	17.4		

53. Reduction to standard conditions. The following calculation will make clear the various steps in reducing the volume of a gas measured over water, at any observed temperature and pressure, to the volume that the same mass of gas would occupy if dried, and at the standard temperature of 0° and the standard pressure of 760 mm. of mercury:

DATA

Observed volume.....	100 c.c.
Barometric pressure (uncorrected).....	756 mm.
Temperature, C.....	20°
Difference of water level (Fig. 36).....	52 mm.

The difference of level being 52 mm. of water column, the equivalent mercury column is $52 \div 13$, or 4 mm. Since the level of the water in the measuring tube is higher than the level in the cylinder, the 4 mm. must be *subtracted* from the barometric pressure.

From the table above the pressure of water vapor for 20° is seen to

be 17.4 mm., and this also must be subtracted from the barometric pressure. Hence, the actual pressure under which the gas is measured becomes:

$$756 - 4 - 17.4 = 734.6 \text{ mm.}$$

Thus the corrected original pressure is 734.6 mm.

The absolute temperature corresponding to 20° C. is 293. Hence, the calculation to standard conditions becomes:

$$\text{Final volume} = 100 \times \frac{273}{293} \times \frac{734.6}{760} = 90.19 \text{ c.c.}$$

The student will find his chief difficulty in making up his mind which quantities to put into the numerator and which into the denominator of the temperature fraction and of the pressure fraction. In the present problem, the gas in being changed to standard conditions would be *cooled* from 20° to 0°, and this cooling would evidently *reduce* its volume; hence the temperature fraction must be $\frac{273}{293}$. Moreover, the gas would be *compressed* from 734.6 mm. to 760 mm. pressure, and this also would *reduce* the volume; therefore the pressure fraction must be $\frac{734.6}{760}$.

SUMMARY

The volume of a mass of gas varies inversely as the pressure upon it. This is **Boyle's Law**.

The temperature of a body deprived of all heat would be -273° C. This is the **absolute zero**.

Hence the **absolute temperature** is obtained by adding 273 degrees to the centigrade temperature.

The volume of a mass of gas is proportional to its absolute temperature. This is **Charles' Law**.

Zero centigrade is chosen as **standard temperature**, and **760 millimeters** of mercury as **standard pressure**. When nothing is said about the temperature and pressure under which a gas is measured, these **standard conditions** are understood.

Two gases when brought into contact will automatically produce a uniform mixture. This is the **diffusion of gases**.

A crystal is a solid, bounded by plane surfaces, which owes its form to the internal forces of the substance and not to an external shaping process imposed upon it.

EXERCISES

1. 10 liters of gas at a pressure of 743 mm. will occupy what volume at 720 mm.?

2. 18.5 c.c. of nitrogen are measured under a pressure of 745 mm. What will the volume be at 760 mm.?

3. A liter of oxygen is measured at 760 mm. What will it measure at 748 mm.?

4. Calculate the absolute temperatures corresponding to each of the following centigrade temperatures: (a) 13° ; (b) 274° ; (c) -50° ; (d) -273° .

5. What volume will a liter of air measured at 0° occupy at 100° ?

6. 5 liters of oxygen at 0° occupy what volume when the temperature is changed, (a) to 10° ? (b) to -10° ?

7. 25 c.c. of nitrogen at 15° will have what volume at the standard temperature?

8. I have 500 c.c. of nitrogen at 13° . What will the volume become at 65° ?

9. 600 c.c. of oxygen at 28° will have what volume at -14° ?

10. 67 liters of air are heated from -30° to 60° . What is the new volume?

11. 100 c.c. of oxygen at -15° and 740 mm. will occupy what volume at standard conditions?

12. What volume will 48 c.c. of nitrogen at standard conditions occupy at 18° and 730 mm.?

13. 25 liters of a gas at standard conditions are cooled to -10° and the pressure reduced to 723 mm. What is the final volume?

14. 271 c.c. of nitrogen at 269° and 900 mm. are cooled to -51° and the pressure is reduced to 666 mm. Calculate the final volume.

15. 112.1 c.c. of air, measured over water at 16° and 744 mm., will occupy what volume dry and at standard conditions?

16. 11.41 c.c. of gas are measured over water at 14° and 743 mm. Calculate the volume when dry and under standard conditions.

17. 150 c.c. of oxygen are measured over water at 21° and 761 mm. Reduce the volume to standard conditions.

18. 20 c.c. of air are measured over water. The level of the water in the graduated tube is 26 mm. above that in the cylinder. The temperature is 19° and the barometer stands at 757 mm. Reduce the volume to standard conditions.

19. 30 c.c. of nitrogen are measured over water. The difference of level is 39 mm., that in the graduated tube being higher. The temperature is 22° and the barometric pressure 755 mm. Reduce to standard conditions.

CHAPTER VI

MOLECULES

54. The micron. Recent investigation has proved that matter has a granular structure, somewhat similar, on a small scale, to that of a heap of baseballs or a pile of sand. In other words, matter is composed of *particles*, and we have now to study the particles of which all substances consist. These particles are called **molecules**.

In dealing with such very small distances as the diameter of molecules and the spaces between them, it is necessary to employ a very small unit. A convenient unit is the *thousandth of a millimeter* (0.001 mm.), which has received the name of the **micron**. In order to conceive some idea of the length of this unit we may reflect that the thickness of a dime is about a millimeter. Suppose a dime to be cut into a thousand circular slices; the thickness of each of these very thin plates would be 1 micron. That of the tin foil used for wrapping chocolate is about 10 microns. Gold can be beaten into leaf the thickness of which is only 0.1 micron.

55. The molecular theory. A liter of air can be crowded by increased pressure into a volume of about 1 c.c. There are two ways, and only two, of interpreting this fact:

1. The actual *matter* of the air is compressed until it occupies only about one thousandth of the original space. This interpretation assumes that the air is *continuous*—in other words, that it really fills the space which it appears to fill, but it is capable of enormous compression under increased pressure, as well as expansion when its temperature is raised. The doctrine that matter is continuous explains none of the known facts of chemistry or of physics and has pointed the way to no achieve-

ments in discovery or invention. It has, therefore, disappeared from scientific thought.

2. The matter of the air did not really fill the volume of a liter in the first place. The air is composed of molecules with large spaces between them. Under pressure the molecules are pushed more closely together; the matter becomes more closely packed.

This is the **molecular theory**. It explains, in a simple and satisfactory way, all the facts of chemistry and physics, and it has led to discoveries and inventions without number. Moreover, the existence of molecules has recently been demonstrated by such direct evidence that it has ceased to be a theory and has become a fact.

56. Dimensions of the molecules. If 10,000 of the molecules of the air were laid side by side, the line would be 1 micron in length. Hence, it would require 10,000,000 of them to make a line of a length equal to the thickness of a dime, and 250,000,000 laid in contact to make a line 1 in. in length. Yet the number of molecules in 1 c.c. of air is so great that, laid side by side, they would girdle the earth at the Equator a hundred times. In weight, one of these molecules would bear about the same relation to the human body that the latter does to the sun. There are more molecules in a single drop of water than there are drops in the Atlantic Ocean. One milligram of common salt, which is as small a quantity as can be seen with comfort, contains 12 billion billions of molecules.

The average distance between the molecules of the air is about $\frac{1}{10}$ of a micron, which is about the thickness of the most delicate gold leaf. This distance between the molecules of the air is, therefore, about a thousand times as great as the diameter of the molecules themselves.

57. Motion of the molecules. How then do we explain the power of a liter of air to fill any vessel in which it is placed, however large? At first it would seem that, even in a liter bottle, a liter of air would settle until the molecules were in

contact, forming a thin layer upon the bottom and leaving a vacuum above.

There is an easy answer to this question. The molecules would indeed settle if they were at rest. But they are not at rest. They are in rapid, continual motion in straight lines. Each molecule moves until it strikes another molecule or the wall of the containing vessel, whereupon it rebounds in some new direction. Imagine a lot of billiard balls rolling about and rebounding from each other and from the cushions of the table. The table must be thought of as entirely frictionless and the cushions and balls as perfectly elastic, so that no energy is lost in motion or after a rebound; under such conditions the motion will keep up forever. Finally, imagine the movement to take place in three dimensions, instead of merely on a flat surface. Or, think of a swarm of angry, tireless bees shut up in a box. It is such motion as this that keeps the molecules of a gas distributed evenly through the whole of any space open to them.

Every molecule of the air we breathe is moving in a straight line with about the speed of a rifle bullet. It strikes other molecules 5 billion times in a second, each shock changing the direction of its motion. Between these encounters, it moves an average distance of 0.1 micron, which is about one thousand times its own diameter.

The drops of water or of oil in the spray produced by an ordinary atomizer are about 1 micron in diameter. Imagine such a drop, floating in air, to be fairly struck below by a molecule moving vertically upward. The impact would lift the little sphere through its own diameter, and the motion would be *perfectly visible under the microscope*. Although we cannot see the moving molecule itself, we can easily see the effect of the shock when a moving molecule strikes a minute visible particle suspended in a gas or a liquid.

58. Boyle's law. In our illustration of the billiard balls, it is plain that there would be a constant succession of violent

blows against the cushion of the table. If the balls were very numerous, these blows would be so frequent that they could not be perceived separately. Instead of a series of shocks, they would produce the effect of a steady pressure.

The pressure of a gas is the aggregated impact of the bombardment of its molecules against the surface pressed. If a liter of air is crowded into the space of half a liter, there must be twice as many molecules in each cubic centimeter as before. Hence, twice as many molecular blows will be delivered per second against every square centimeter of the surface in contact with the gas; in other words, the pressure will be doubled. This is *Boyle's Law*, that the volume of a gas varies inversely as the pressure.

59. Diffusion. Diffusion of gases, referred to in the preceding chapter, is a direct result of the motion of the molecules. The forward movement of the molecules of oxygen in our illustration (Fig. 33) carries them up into the nitrogen, while the molecules of nitrogen move downward. Other pairs of gases act similarly. Diffusion, assisted by the winds, keeps the gases of the atmosphere uniformly mixed, though their densities are very different.

60. Charles' Law. This incessant molecular motion is what is commonly called **heat**. The hotter a gas grows, the more heat energy there is in it, the more violent the molecular agitation becomes. But motion is what keeps the molecules apart; and the more rapid their motion, the farther apart, on the average, they will be, and the greater the volume the gas will occupy. Hence *Charles' Law*, that the volume of a gas is directly proportional to the heat energy in it, that is, to its absolute temperature.

61. Molecular motion in liquids. So far, we have confined ourselves to gases, but liquids and solids also are composed of molecules, and, at any temperature above the absolute zero, their molecules must be in motion. *Milk* contains very small globules of butter fat suspended in a watery liquid. They are

easily examined under the microscope, through which they look like little glass spheres, of very different sizes, distributed through fluid. But the significant thing about the appearance of milk under the microscope is that the fat globules are in *constant agitation*. The motion of the large globules is sluggish—a mere vibration or trembling, while the smaller ones move more rapidly, and through longer distances. The cause of this wonderful, ceaseless movement will be apparent from the preceding sections. The moving water molecules are constantly colliding with the fat globules and pushing them about, and the smaller globules move farther because, being lighter, they are more easily pushed.

The same agitation is perceptible whenever any finely divided substance is suspended in water. Many pigments, for instance, are ground so fine in the ordinary processes of manufacture that when suspended in water each particle of the pigment is thrown into violent agitation by the innumerable water molecules that collide with it. All that is necessary is to make the particles so small that the impact of the water molecules is sufficient to move them; then they at once begin to show the effects of the collisions, “just as a cork follows better than a large ship the motion of the waves of the sea.”

62. Molecular motion in solids. The facts of the preceding section show that the molecules of a liquid behave in about the same way as those of a gas. The chief difference is that in the liquid the molecules are more crowded, and the average distance travelled between successive collisions is much shorter. But in neither liquid nor gas is there any place in which a molecule *belongs* and to which it always returns.

There are, however, many facts indicating that a molecule that forms part of a *crystalline solid* does not readily desert its position and move to some new locality. Consider, for example, a jewel, say an emerald, with a figure engraved upon it. If the molecules were, like those of a gas, in constant, *undirected* motion from their original positions to all other parts of the

stone, the lines of the design would become blurred and would ultimately disappear. But engraved gems on which the work must be at least 5,000 years old have frequently been found in Egyptian tombs, and the lines are as sharp as though the cutting had just been completed. A still more striking proof is found in the prehistoric drawings made by the cave dwellers on slabs of stone. These must be at least ten times as old as the jewels just referred to, yet they show no evidence of blurring due to molecular motion.

Finally, crystals the edges of which are still perfectly sharp and definite are found in the most ancient rocks. These crystals must be at least a thousand times as old as the oldest human handiwork, and their perfect preservation is a convincing proof of the permanency of the position of the molecules in crystalline solids. This does not mean that the molecules of the crystals are *at rest*, which would be possible only at the absolute zero, but that they *vibrate* within certain definite limits about a position to which they always return.

SUMMARY

The **micron** is the unit employed in measuring very small distances. It is equal to 0.001 millimeter, which is about one one-thousandth of the thickness of a dime.

All matter is composed of particles called **molecules**.

The molecules of the same substance are all *exactly alike*, but the molecules of two different substances are *different* in weight, composition, and other properties.

The **diameter** of a molecule is about *one ten-thousandth of a micron*.

The average *distance* between the centers of two molecules in gases at ordinary pressure and temperature is *one-tenth of a micron*. This distance is the *same in all gases* under the same conditions. It is independent, therefore, of the composition of the gas.

At all temperatures above the absolute zero the molecules of all substances are in rapid motion. This fact provides a simple explanation of the diffusion of gases and of the laws of Boyle and Charles.

Heat is molecular motion. Molecular motion can be studied under the microscope by using suspended particles small enough to move when struck by a molecule.

In liquids and gases the molecules are in *complete disorder*. In *crystals* the molecules have an *orderly arrangement*, which is permanent although the molecules are in rapid *vibration*.

EXERCISES

1. What is a micron?
2. Give a brief summary of our knowledge of the dimensions and motions of the molecules.
3. Apply the fact of molecular motion to explain the diffusion of gases and the laws of Boyle and of Charles.
4. How can the effect of the motion of the molecules be rendered visible?
5. Explain the differences in the movements of the molecules in gases, liquids, and solids.
6. Do the molecules of crystalline solids move permanently from one part of the solid to another? Give facts to support your answer.
7. What would be the condition of the molecules at the absolute zero?
8. Why does heat convert a liquid into a vapor?
9. If you wanted to liquefy a gas, would you heat it or cool it? Compress it or lower the pressure upon it? Why?

REVIEW QUESTIONS

1. Why is it necessary to specify the temperature and pressure under which a gas is measured?
2. What is the effect of water vapor upon the volume of a gas.

CHAPTER VII

HYDROGEN

63. The interaction of zinc and steam. We have seen that powdered *zinc*, when heated in the air, is converted into *zinc oxide*. The same substance is produced when powdered zinc is heated in *steam*. The experiment is shown in Figure 37. Steam, made by boiling water in the flask, is passed over heated zinc dust in a hard-glass tube. The gas issuing from this tube is collected over water in an inverted cylinder.

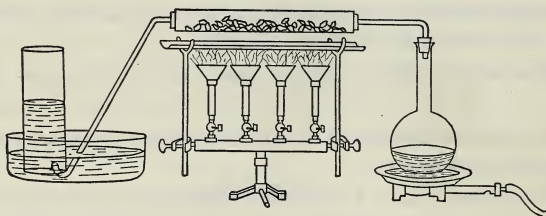
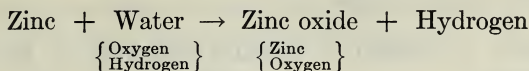


Fig. 37. Apparatus for passing steam over heated zinc.

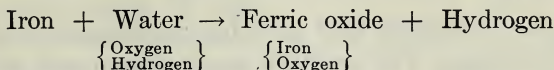
The zinc changes to white zinc oxide, which proves that *oxygen is one constituent of water*. In the cylinder a colorless gas collects, which proves, when tested with a flame, to be combustible. Since zinc is an element, this gas can come only from the steam, and it also, therefore, must be a constituent of water.

This new gas is called **hydrogen**, a name which means "producer of water," and which was given to the gas by Lavoisier. We can write out, in words, a kind of equation for the experiment, which will make clear the chemical process. The names of the elements placed below in braces indicate

the composition of the substances named above them. The arrow is to be read "yields" or "produces."



Iron liberates hydrogen from steam in the same way as zinc.



This is one of the methods used in the commercial production of hydrogen on a large scale.

64. Behavior of potassium and sodium with water. There are metals that act vigorously on water in the cold. When a bit of the soft, waxy metal **potassium** is thrown upon water, hydrogen escapes with such energy that the gas ignites, and continues to burn until the potassium is all consumed (Fig. 38).

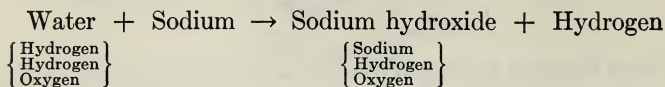
Sodium interacts with water less violently than potassium. For experimental proof, a small quantity of sodium is forced into a lead tube that has been hammered shut at one end. This is dropped into water, and an inverted cylinder filled with water is held over it. Bubbles rise through the cylinder, and when enough of the gas has collected, it can be identified as hydrogen by burning it.

Only *half* of the hydrogen of the water that enters into the chemical change, however, is liberated in this experiment. The other half of the hydrogen, and all of the oxygen of the water, combine with the sodium to form a white compound called *sodium hydroxide*, commonly termed "concentrated lye," which dissolves in the additional water present and so escapes observation. It can be recovered by evaporating the water to dryness. It seems, then, that the hydrogen of the water

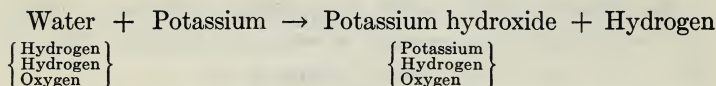


Fig. 38. Action of potassium on water.

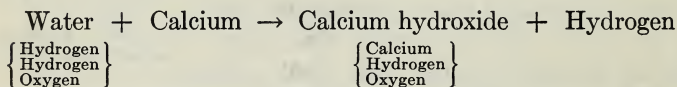
divides in two portions, one of which escapes, while the other remains, united with the sodium and the oxygen. We may write the equation thus:



Similar statements hold good for the interaction of water with potassium. The products are hydrogen and *potassium hydroxide*, which is a white solid resembling sodium hydroxide. The equation may be written thus:



The experiments with sodium and potassium may be dangerous to the eyes and should not be undertaken without skilled supervision. The metal *calcium*, however, liberates hydrogen from water in the same way, though more slowly, and the experiment is quite safe. The equation is similar to those just given:



Calcium hydroxide is ordinary *slaked lime*. It does not dissolve freely in water, and it is therefore obtained in this experiment as a white powder, suspended in the liquid.

65. The electrolysis of water. Water is placed in the glass dish of Figure 39. The two tubes are filled with water and inverted over two pieces of platinum foil, to each of which a wire is attached. These pieces of platinum serve to conduct an electric current into and out of the liquid. They are called the **electrodes**, positive and negative as marked in the illustration. As a source of current the 110-volt direct-current circuit

found in most schools is suitable, but if this is used a 16-candle-power lamp should be placed in series with the apparatus.

When the circuit is completed, the lamp does not light up, and the apparatus shows no indication that a current is passing, for water is almost a non-conductor of electricity. But when a little *sulphuric acid* is added to the water, the lamp glows and bubbles of gas rise from both electrodes. The sulphuric acid, however, merely carries the current through the liquid, and is found in it after the experiment unchanged in quantity. It is the *water* that is decomposed.

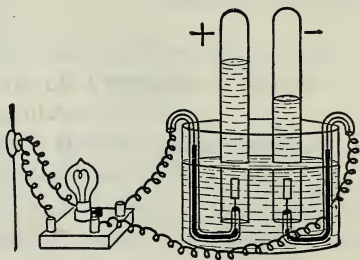


Fig. 39. Electrolysis of water.

The gas that collects over the positive electrode proves, upon application of the spark test, to be *oxygen*. Over the negative electrode hydrogen collects, as can be shown by applying a flame to the gas. *The volume of the hydrogen is twice that of the oxygen.* Decomposition of this kind, brought about by the electric current, is called **electrolysis**.

66. Preparation of hydrogen.

We have seen that water yields hydrogen when brought into contact with metals like sodium or zinc. These methods are not suitable for making the gas in the laboratory, for the use of sodium is dangerous and expensive, and zinc acts only upon steam, which makes its use in-

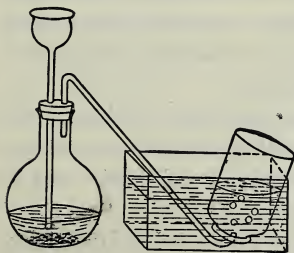
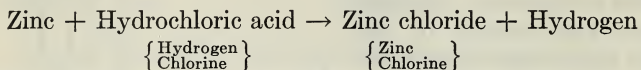


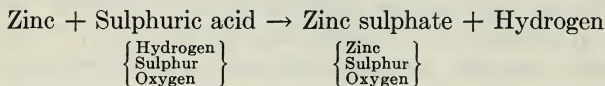
Fig. 40. Preparation of hydrogen by interaction of an acid with zinc.

convenient in a laboratory method. Water, however, is not the only hydrogen compound that gives off the gas when

treated with zinc. *Hydrochloric acid*, when properly diluted with water, interacts with zinc in the cold, yielding hydrogen. The apparatus is shown in Figure 40. Hydrochloric acid is a compound of hydrogen and *chlorine*. In the chemical change the chlorine combines with the zinc to form *zinc chloride*, the hydrogen escaping:



Sulphuric acid, which is a compound of hydrogen, sulphur and oxygen, is often used instead of hydrochloric acid. When sulphuric acid is used, the second product is *zinc sulphate*, a white compound of zinc, sulphur, and oxygen, which can be recovered by evaporating the liquid in the gas-generating bottle to dryness:



Dangerous explosions may result in this experiment when students attempt to light the hydrogen at the exit tube of the apparatus. This should never be done without consulting the teacher beforehand. The burner upon the desk should be extinguished before the preparation of hydrogen is begun.

All acids are hydrogen compounds, and many of them yield the gas by interacting with zinc and with various other metals. The choice of zinc and hydrochloric acid or sulphuric acid is dictated by convenience and economy.

67. When hydrogen is needed frequently in small quantities, the *Kipp generator*, shown in Figure 41, is convenient. The zinc is placed in the middle bulb, and hydrochloric acid, diluted with an equal volume of water, is poured in at the top. When the acid reaches the zinc, interaction begins and hydrogen escapes. When the gas is no longer needed, the glass stopcock

on the exit tube is turned off, as shown in the illustration. As soon as the pressure of the hydrogen has forced down the level of the acid until it is no longer in contact with the zinc, the interaction ceases, and the apparatus can be put away until hydrogen is again required, when it can be obtained by merely opening the stopcock.

68. Physical properties. Pure hydrogen is colorless, odorless, and non-poisonous. The gas prepared by the interaction of acids and zinc owes its odor to impurities which would make it dangerous to take into the lungs. Hydrogen is by far the lightest

of gases, a liter of it weighing only 0.09 gram. It is, therefore, less than one-fourteenth as dense as air, and about one-sixteenth as dense as oxygen. The solubility of hydrogen in water is very small: 100 cubic centimeters of water dissolve 2 cubic centimeters of the gas under standard conditions.

By the application of great cold and pressure, hydrogen has been liquefied. Liquid hydrogen is colorless. Being only one-fourteenth as dense as water, it is the lightest of liquids. It boils at -253°C. (20° abs.), and a vessel filled with it becomes covered with a layer of solid air, condensed by the great cold. When the evaporation of liquid hydrogen is aided by an air pump, the temperature falls to -257°C. , at which point the liquid freezes to an ice-like mass. This solid hydrogen is the lightest of solids, being only about one-thirteenth as dense as water.

Finely divided platinum will absorb more than 100 times its volume of gaseous hydrogen, with the production of much heat. This fact is utilized in the self-lighting Welsbach gas

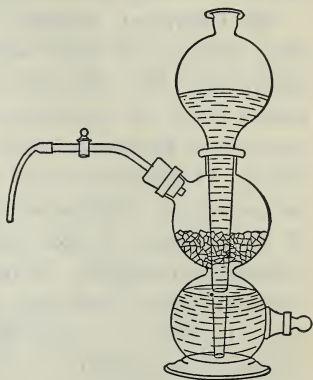


Fig. 41. Kipp hydrogen generator.

mantle. A little ball of spongy platinum is attached to the mantle. Illuminating gas is partly hydrogen. When the gas is turned on, the absorption of the hydrogen by the platinum produces a temperature high enough to ignite the gas.

69. Chemical conduct. Unlike oxygen, hydrogen shows little tendency to unite with the metals. Its conduct towards non-metals, like chlorine, nitrogen, and sulphur, will be discussed later in connection with those elements. The chief property of hydrogen which interests us at present is its *combustibility*, which is due to its energetic union with oxygen at high temperatures. Hydrogen burns with a flame which, because of the absence of solid particles, is non-luminous and almost invisible in daylight. It has a temperature of $2,000^{\circ}\text{C}$., which is much higher than that of the hottest part of the Bunsen flame ($1,600^{\circ}$). A hydrogen flame burning in oxygen has a temperature of $2,500^{\circ}\text{C}$. Such a flame will easily melt platinum, fire clay, and asbestos. Gold and silver vaporize in it, yielding dense smoke. The production of this flame by means of the oxy-hydrogen blowpipe has already been described in Chapter IV.



Fig. 42. Hydrogen burns but will not support combustion.

A mixture of hydrogen and oxygen *explodes* on the application of a flame. The most violent explosion occurs when the mixture contains twice as much hydrogen by volume as oxygen. A favorite lecture experiment is to fill with this mixture a small flask, about which a towel is carefully wrapped to prevent danger from flying glass. When the gas is ignited with a flame, the flask is pulverized by the explosion. Mixtures of hydrogen with air explode less violently, but with quite sufficient energy to wreck the apparatus. It is for this reason that it is dangerous to light the gas at the exit tube of the hydrogen apparatus. Unless all air has been expelled, an explosion will result.

Hydrogen will not *support combustion*. When a lighted candle, fastened to a wire, is thrust up into an inverted bottle filled with hydrogen (Fig. 42), the gas takes fire, but the candle is extinguished. It is relighted when withdrawn through the burning gas at the bottom of the bottle.

The product of the combustion of hydrogen in oxygen or in air is *water*, as was first shown by *Cavendish*. With the appa-

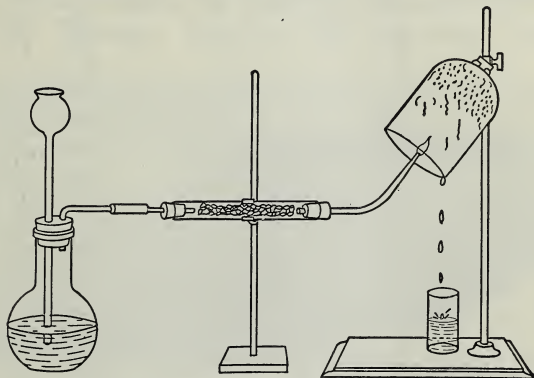
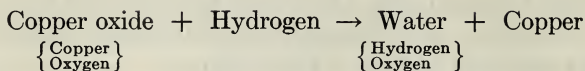


Fig. 43. Synthesis of water by burning hydrogen in air.

ratus shown in Figure 43, 20 to 30 c.c. of water can easily be produced in a short time. Hydrogen from a generator is thoroughly dried and burned at the mouth of a cold, dry bell jar. Almost immediately water vapor begins to condense on the jar and in a short time drops of water run down the sides.

Hydrogen removes oxygen from the oxides of many of the metals when heated to a red heat, forming water and liberating the metal. Thus, black copper oxide, when heated in hydrogen in the manner shown in Figure 44, is converted into a red mass of copper, while water collects in the cool portion of the tube. *Great care must be taken to make sure that all air has been expelled from the gas bottle before heating*

the copper oxide. The chemical change may be expressed as follows:



The removal of oxygen from an oxygen compound is called **reduction**. The oxides of the familiar *heavy* metals,

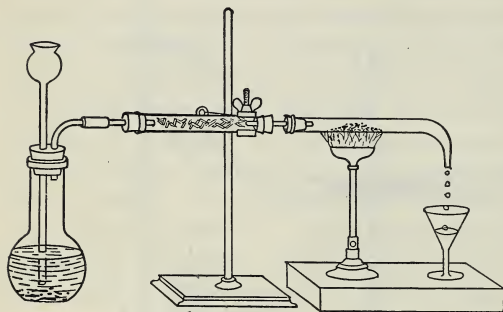


Fig. 44. Reduction of copper oxide by hydrogen.

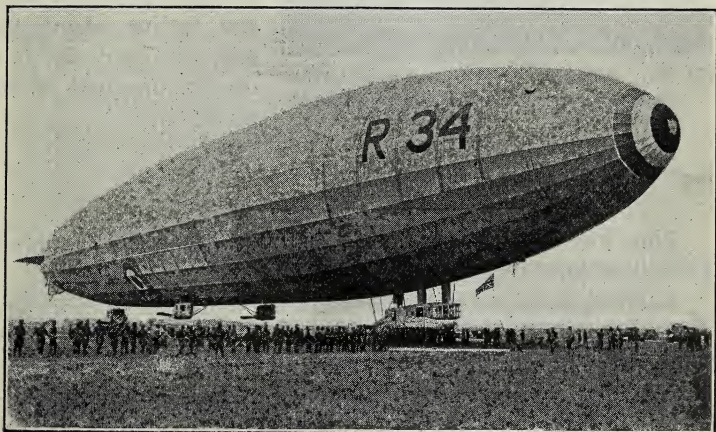
like iron, copper, tin, lead, mercury, etc., are reduced when heated in hydrogen. The oxides of *light* metals, such as magnesium, aluminum, calcium, sodium, and potassium, are not affected by it.

70. Uses of hydrogen. The application of the hydrogen flame to the production of high temperatures has been noted. Many important gaseous fuels, for instance, producer gas, water gas, and illuminating gas, consist partly of hydrogen. On account of its lightness hydrogen is employed for filling balloons and airships.

During the World War lard and other fats became scarce and expensive. Cottonseed oil when heated under pressure with hydrogen, in the presence of finely divided nickel as a catalytic agent, combines with 1 per cent of its weight of hydrogen and passes into a solid resembling lard. The cooking fat sold under the name "Crisco" is made in this way. The process is known as *hydrogenation*. It is also employed to prepare fats suitable for the manufacture of soap. Thus, fish

oil has a most unpleasant smell, but combination with hydrogen converts it into a solid fat which is odorless and quite fit for the soapmaker.

71. Industrial preparation of hydrogen. The most important method of producing hydrogen on a large scale is the electrolysis of water. The process is carried out in an iron cylinder about 3 ft. in diameter and 4 ft. deep. The wall of the cylinder forms the negative electrode; here is liberated the hydrogen, which is then led away through a



Photograph from World Wide Photos.

Fig. 45. The British hydrogen dirigible R 34, the first airship to cross the Atlantic.

tube in the cover to a pump which compresses it into steel cylinders for the market. The positive electrode, at which the oxygen is liberated, is a perforated iron cylinder which hangs from the cover into the liquid. It is surrounded by a diaphragm of asbestos cloth to prevent the two gases from mixing. The oxygen, like the hydrogen, is compressed into steel cylinders for sale. Sodium hydroxide is dissolved in the water to make it conduct the

electric current, serving the same purpose as the sulphuric acid in our experiment.

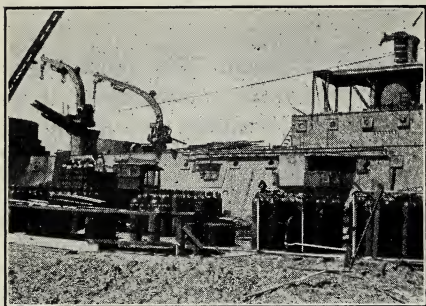


Fig. 46. Cylinders of hydrogen and oxygen assembled for the demolition of a United States cruiser.

Like the latter, it remains unchanged in the liquid. Sulphuric acid cannot be used, as it acts rapidly on iron and would destroy the apparatus. Both gases are quite pure, the oxygen testing about 98 per cent, and the hydrogen, upwards of 99 per cent.

SUMMARY

Zinc, iron and other metals, when heated in steam, combine with the oxygen of the steam, liberating **hydrogen**.

Sodium, in the cold, liberates half the hydrogen from water. The other product is *sodium hydroxide*. The action of **potassium** and of **calcium** upon water is similar to that of sodium.

When the electric current is passed through water containing sulphuric acid, the water is decomposed, 2 parts by volume of hydrogen and 1 part by volume of oxygen being liberated. The sulphuric acid remains unchanged, and other substances can be used in place of it.

Hydrogen is prepared in the laboratory by the action of hydrochloric acid or of sulphuric acid on zinc.

By great cold and pressure hydrogen has been liquefied, and the liquid has been frozen.

Hydrogen burns in air or in oxygen, producing *water*. It also removes the oxygen from many metallic oxides, yielding water and the metal.

Hydrogen is used in filling airships and balloons, in producing high temperatures, and in converting oils into solid or semi-

solid fats. For these purposes it is made by the **electrolysis** of water, by the action of iron on steam, and by other methods.

EXERCISES

1. Compare the interaction of zinc and of sodium with water.
2. Describe the electrolysis of water (a) as a lecture experiment; (b) as an industrial process.
3. Discuss the interaction of zinc with hydrochloric acid and with sulphuric acid. What becomes of the zinc compound produced in each case, and how can it be recovered?
4. Explain the Kipp apparatus.
5. What is the principle of the self-lighting gas mantle?
6. How can water be obtained from its elements?
7. In what way does hydrogen act upon oxides?
8. How is cottonseed oil converted into a solid, edible fat?
9. What element is present in all *acids*?
10. In the industrial electrolysis of water it has occasionally happened that a steel cylinder intended for compressed hydrogen has been filled with a *mixture* of hydrogen and oxygen. What would be the result of attempting to use such a cylinder with the oxy-hydrogen blowpipe?
11. What would be the effect of lighting the hydrogen at the end of the delivery tube of a generator before all the air had been expelled from the apparatus?
12. Could the flame of burning hydrogen be employed as an illuminant? Could it be used with a Welsbach mantle? Would it be suitable for cooking?
13. What fact regarding the composition of the air is proved by burning hydrogen in air and identifying the product?
14. Make a tabular statement of the similarities and points of difference between hydrogen and oxygen.
15. What feature in the chemical conduct of hydrogen is a grave objection to its use for filling balloons and airships?

REVIEW QUESTIONS

1. Classify into physical and chemical changes the following: the evaporation of gasoline, the burning of gasoline, the crushing of glass, the electrification of glass by rubbing, the striking of a match, the tarnishing of silver, the decay of food products.

2. Explain the part played by the study of the action of air on heated mercury in laying the foundations of chemistry.

3. Explain the precise meaning of the *symbol* of an element. Can a compound or a mixture have a symbol?

4. Name the first five elements in order of abundance.

5. Explain how slow oxidation can develop into spontaneous combustion.

6. What is *catalytic action*?

7. Explain the method of reducing to standard conditions the volume of a gas measured over water and at the temperature and pressure of the school laboratory. The level of the water is supposed to be higher in the graduated tube.

8. How can heat be made visible under the microscope?

9. What is a molecule? Summarize the facts that have led chemists and physicists to believe in their existence.

10. What is *reduction*? When copper oxide is reduced by hydrogen, is the hydrogen oxidized at the same time? Can reduction ever occur without oxidation?

CHAPTER VIII

WATER AND ITS PURIFICATION

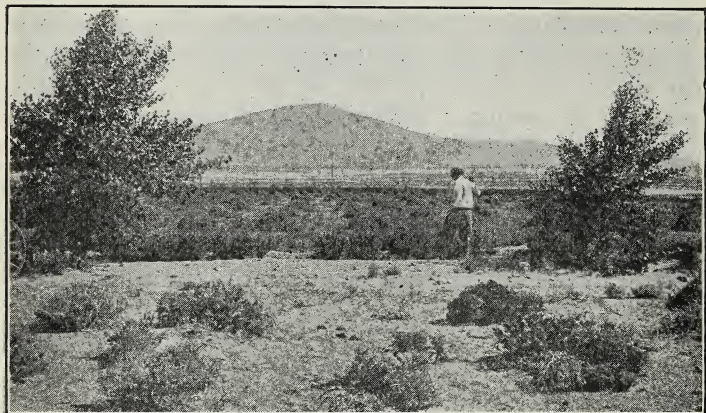
72. Water in nature. Water in the form of ice perpetually overlies the polar regions of our planet, while liquid water covers three-fourths of its remaining surface. This water is in constant circulation. It is evaporated from the oceans by the heat of the sun and blown over the land, upon which, when condensed by cooling, it falls as rain, which largely finds its way again into the ocean.

Rain is the purest natural water, but even while in the air it absorbs gases and becomes contaminated with dust and with bacteria. When it reaches the surface of the earth, the water at once begins to take up mineral matter from the soil and from the rocks. The average river water of the eastern United States contains about 60 parts of dissolved solids per million parts of water (0.06 gram per liter). Many western rivers contain far more than this.

Spring water and well water are richer in dissolved matter than river water, varying from 100 to 500 parts per million. *Mineral waters* are spring waters which carry such large quantities of solids in solution that they have a marked flavor and a special action of some kind on the body. Dissolved solids, chiefly salt, make up 3.5 per cent of sea-water, while the waters of the Great Salt Lake and the Dead Sea contain upwards of 25 per cent of mineral matter—so much that aquatic life does not exist in them.

73. The water in the soil. When rain falls, the moisture sinks into the soil, carrying with it plant food in the form of dissolved mineral matter, part of which, if the rainfall be excessive or the soil sandy, may be lost in the “run-off” or

drainage. When the rain ceases, evaporation begins at the surface, and the soil water begins to rise, carrying with it dissolved plant food which accumulates in the surface soil. This power possessed by soils of drawing up water from their lower depths extends down 6 or 7 ft. If the lower half of a towel be immersed in water, it will shortly be found that the rest of the towel has also become wet. The soil acts in exactly the same way. The soil water, therefore, is ceaselessly in motion.



Courtesy of the Reclamation Service.

Fig. 47. An alfalfa field reclaimed from the surrounding desert and made fertile by irrigation.

About 700 lb. of water is evaporated annually from each square foot of the average field. Evidently, if the ground were covered, this evaporation would be checked. When the surface soil is thoroughly harrowed to a depth of two or three inches on a dry day, a layer of dust is formed which is very effective in reducing evaporation and thus conserving water for the crops. This is one of the principles of the system of "dry farming" which has been so successful in the semi-arid regions of the United States.

The circulation of the soil water has a most important function in bringing plant food within reach of the roots. If the soil water were stationary, 20 times as much fertilizer as is now needed would be required to supply the plants with the same amount of food. Too much clay (over 16 per cent) in the soil obstructs the circulation of the water and makes the land difficult to work.

74. Water in food products. Surprising quantities of water are contained in plant and animal matter. It constitutes two-thirds of the weight of the human body as a whole. The bones contain 50 per cent; the muscles, 75 per cent; and the gray matter of the brain, 85 per cent. The percentages of water in some important food products are given in the following table:

WATER IN FOOD PRODUCTS

ANIMAL		VEGETABLE	
	Per cent		Per cent
Bacon.....	20	Apples.....	85
Beef.....	73	Asparagus.....	94
Codfish.....	83	Beets.....	88
Eggs.....	74	Cabbage.....	92
Ham.....	53	Celery.....	95
Milk.....	87	Potatoes.....	78
Salmon.....	65	Strawberries.....	90

75. The water vapor of the air. As a colorless, invisible vapor, water forms an important constituent of the air, which contains, on an average, 10 grams of water per cubic meter. In the whole atmosphere the quantity of water is estimated to amount to 50 billion tons, enough to form a lake which would cover 12,000 square miles to a depth of 1 mile. Life upon the earth is entirely dependent upon the presence of water vapor in the atmosphere, since without it there could be no rain.

Water vapor is *light*—only a little more than half as dense as dry air. It is, therefore, as light as the illuminating gas formerly used in balloons. Hence, air that becomes moist by taking

up water from the ocean rises to the higher, colder levels of the atmosphere, where the vapor condenses to fine drops of liquid, which form visible clouds. Clouds are usually formed far above the surface of the earth. If water vapor were heavier than air, they would form at the earth's surface, which would be bathed in a perpetual fog.

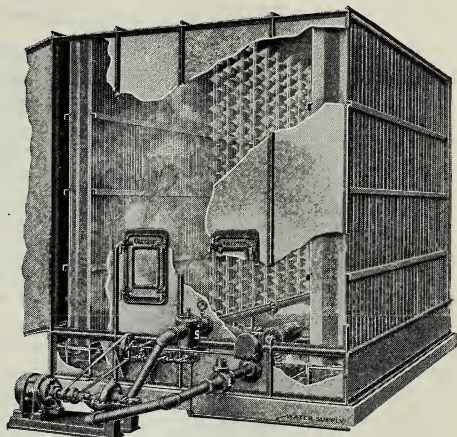
Out of doors, throughout the year, the air contains on an average about three-quarters of the amount of moisture that would be required to *saturate* it so that it would take up no more. This condition would be expressed in a weather report by the statement that the **humidity** was 75 per cent. The amount of water vapor in the air, however, varies greatly. High humidity in summer adds greatly to the prostrating effect of the heat, because it prevents cooling by the evaporation of the perspiration.

Indoors in winter the humidity of the air of our dwellings is about 30 per cent. This means that in winter we habitually breathe air dryer than is found in any habitable portion of the surface of the earth. Unfortunately the contrivances sold to remedy this condition, such as pans of water in hot-air heaters and on radiators, are useless. It would require the evaporation of a hundred gallons of water each day of winter properly to moisten the air of a house of ordinary size. About the only thing that can be done at present to remedy the dryness of the air of our houses is to control the temperature. When the air of a room is heated to a temperature higher than is needed for comfort, the humidity rapidly decreases. Thus, the risk of injury from excessive dryness of the air is much greater if the temperature is carelessly allowed to rise to 80° F. or 90° F. than it is if the rooms are kept at the proper temperature of 68° F. (20° C.).

The amount of water vapor in the air has an important influence on the working of many industrial processes. Confectionery and other products injuriously affected by moisture must be packed and stored in a relatively dry atmosphere

(§ 89). Baking, spinning, and the manufacture of chewing gum are among the many processes which require an atmosphere relatively high in moisture for most advantageous operation. For such industries air may be *conditioned* by artificially controlling the humidity.

Figure 48 illustrates a common type of humidifying apparatus. Air entering the spray chamber at the right is filled with a fine mist and completely saturated. The air leaves the spray chamber at the left through eliminator plates which remove all free and entrained moisture. The air is thus delivered to the distribution system completely saturated



Courtesy of the Carrier Engineering Corporation.

Fig. 48. A common type of humidifying apparatus.

at the temperature of the spray water. Positive humidity control is effected by controlling the temperature of the spray water.

76. Preparation of pure water. Compounds of the four metals *calcium*, *sodium*, *magnesium*, and *iron* make up the chief part of the dissolved matter of ordinary water. These impurities unfit it for laboratory uses. The method of purification depends on the fact that water is converted into steam by raising it to a temperature of 100°C ., whereas the mineral matter does not vaporize at all at that temperature. Hence, the steam, when passed through a cold tube, condenses to form water which is practically pure.

Figure 49 illustrates the principle of the process. The water is heated in a copper vessel *B*, and the steam passes through

A and *C* into the spiral tube *D*, of copper or tin, which is cooled by water circulating outside it. Pure water collects in *O*. The mineral impurities remain in *B*. Glass vessels are

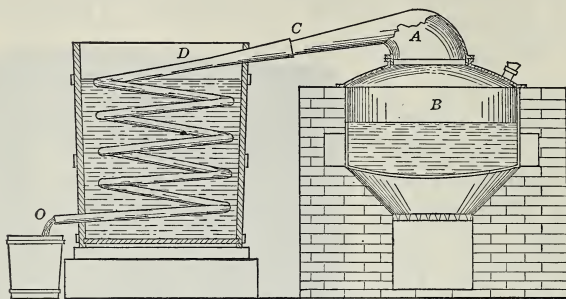


Fig. 49. Distillation of water.

not used because glass dissolves somewhat in water. The process is called **distillation**. It is extensively used for purifying other liquids. The apparatus employed in the laboratory for preparing small quantities of distilled water is shown in Figure 50.

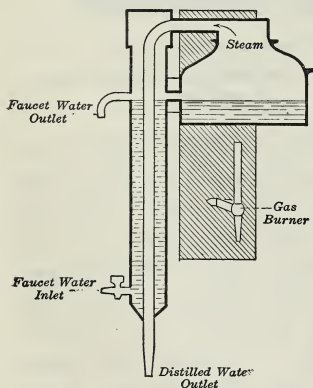


Fig. 50. Laboratory distilled water apparatus.

The student will perceive that distillation on a gigantic scale occurs in nature, and that rain is really distilled water. Rain water, in fact, is pure enough for many purposes, those of the photographic worker for example, but it is not sufficiently pure for the use of the chemist.

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77. Physical properties of water.

Pure water is an odorless, tasteless, and, in thin layers, colorless liquid. In thick layers water is blue. The color is noticeable when a porcelain bath-

tub is filled, and in layers two meters or more in thickness it becomes very distinct. This is the chief cause of the blue color of large bodies of water in lakes and in the ocean. When water is heated, the color changes to green.

The freezing point and the boiling point of water under a pressure of 1 atmosphere are taken as the two fixed points of the centigrade scale. Increased pressure tends to keep the water liquid, for it lowers the freezing point and raises the boiling point. Dissolving salt, sugar, or any other solid in the water has the same effect; the solution freezes at a lower temperature and boils at a higher temperature than water itself.

Water dissolves a greater variety of different solids than does any other liquid. This power is closely connected with the important part played by water in the vital processes of animals and plants.

The quantity of heat required to raise the temperature of 1 *gram* of water 1°C . is the scientific unit of heat. It is called the **calorie** (contraction, *cal.*), or often, more specifically, the *small calorie*. The quantity of heat required to raise the temperature of 1 *kilogram* of water 1°C . is a unit of heat largely used by engineers. It is called the **Calorie** (contraction, *Cal.*), often termed the *large calorie*. Another unit much used by engineers is the quantity of heat required to raise the temperature of 1 pound of water 1°F . This is called the **British thermal unit** (B.t.u.). One Calorie is equal to approximately 4 B.t.u.

The quantity of heat absorbed in warming 1 kg. of water 1° is greater than that required to warm the same amount of any other substance through the same range. Since the body is two-thirds water, this fact makes it easier than it otherwise would be for the body to maintain its constant normal temperature of 37°C .; much heat must be supplied to warm it or withdrawn to cool it, and variations in temperature do not readily occur. The great heat capacity of water also

contributes to the efficient working of hot-water heating systems.

It requires 536 cal. of heat to convert 1 gram of water at 100° into steam, which is more than is absorbed in vaporizing a gram of any other liquid. The fact that unit weight of water is able, when vaporized in the boiler, to carry 536 heat units, and liberate them when the steam condenses in the radiators, is utilized in steam heating.

To melt 1 gram of ice 80 cal. are needed, which is more heat than is absorbed in the melting of a gram of any other solid; hence the efficiency of ice for the absorption of heat in the refrigerator and in the freezing of ice cream.

78. Pure water in the household. A moderate amount of dissolved mineral matter in a water intended for general use is rather advantageous than otherwise. Moreover, few natural waters contain enough animal or vegetable matter to make

them dangerous to health. The main object in the purification of a water for the household is to make it *sanitary*, that is, to remove or destroy the germs of disease which may be present in it. The chief diseases known to be transmitted by water are Asiatic cholera, cholera infantum, dysentery, and typhoid fever; of these, under ordinary conditions, the last is the most important. In 1885 the carelessness of an attendant on a typhoid patient near the town of Plymouth, Pa., contaminated the water supply and caused an epidemic in which there occurred 1,104 cases, with 114 deaths.



Fig. 51. Pas-teur filter.

The surest way to *sterilize* a water in the household is to boil it for at least 10 minutes. It can then be cooled and aerated by pouring it back and forth from one vessel to another to remove the objectionable flat taste which boiled water often possesses. Water treated in this way is perfectly safe, even though it may have been badly contaminated.

Impurities suspended in water, including bacteria, may be removed by **filtration**. The *Pasteur filter* (Fig. 51) consists of a metal case surrounding a cylinder of unglazed porcelain closed at one end. The water is admitted to the space between the two and passes slowly, under the pressure in the mains, through the porcelain to the inside of the cylinder. Bacteria and other suspended matter are filtered out and collect in a slimy layer on the outside of the porcelain cylinder, which should be frequently cleaned with a stiff brush. It should also be sterilized from time to time by heating it to 100° C. or over for 10 minutes. This filter is efficient if properly cared for and kept clean, but many of the small filters sold for domestic purposes are worse than useless.

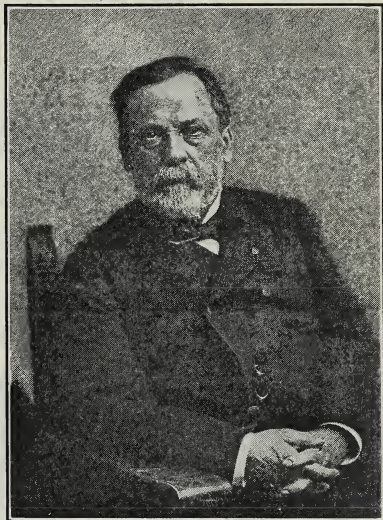


FIG. 52. LOUIS PASTEUR (1822-1895).

79. Purification of municipal water supplies.

Sterilization of water by heat is simple and effective, but it is far too expensive for municipal purposes. The city of Philadelphia, for instance, requires about 200 million gallons of water daily, and to boil such a quantity would involve an expenditure for fuel that would be prohibitive. Sterilization by ozone, already referred to in Chapter IV, has been very successful in Europe. The addition of about one part of *chlorine*

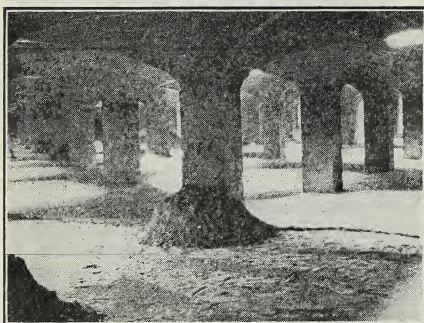
(§ 112) per million parts of water is an effective method of destroying dangerous organisms which is in wide use as an adjunct to filtration and for dealing with water supplies that have suddenly become infected.

Most cities purify their water supplies either by slow sand filtration or by rapid sand filtration. In *slow sand filtration*



Fig. 53. Diagram of a slow sand filter.

the water is allowed to pass through a bed of fine sand about 4 ft. thick, the average diameter of the grains being 0.01 in. (0.25 mm.). The sand rests on a layer of gravel, and the pure water is drained off below. The filter is usually covered to



Courtesy of Hazen, Whipple & Fuller.

Fig. 54. Interior of a filter bed in process of cleaning.

doubt that it is an effective safeguard against the dangers of water-borne disease. If the process is carefully carried out, 99 per cent of the living organisms are removed.

In *rapid sand filtration* the sand is coarser and the water

prevent freezing. The rate of filtration is about 2,000,000 gallons per acre each 24 hours. The filters require cleaning every three weeks. Owing to the slow rate at which the water passes through the bed, a large city requires extensive filters. This is the oldest method of municipal purification, and there can be no

passes through it about fifty times as rapidly. The filter, therefore, will yield over 100,000,000 gallons per acre per 24 hours. *Aluminum sulphate*, which is very similar to alum in properties and composition, is added to the water before it enters the filter; limewater, if necessary, is also added. The effect of the chemicals is to coat the grains of sand with a gelatinous film which detains the bacteria and prevents them from passing through the filter. This, also, is an excellent method of purification and its use is rapidly extending in the United States. The cost of installation is less than that of slow sand filtration on account of the small size of the filters required. The aluminum sulphate does not remain in the water, and there is no sanitary objection to its use, especially as the quantity used is only one part in 70,000 parts of water. The percentage of bacteria removed is about the same as in the slow sand process (98-99 per cent).

SUMMARY

All natural waters contain dissolved mineral matter, chiefly compounds of calcium, magnesium, sodium, and iron. Spring water and well water are richer in solids than river water.

The water in the soil plays a most important part in bringing plant food within reach of the roots.

Stirring up the surface soil on a clear, windy day following a rain forms a layer of dust which checks evaporation and conserves the water in the soil for the use of plants. This procedure, combined with the selection of drought-resisting crops, is the basis of "dry farming."

Food products contain from one-fifth to nine-tenths their weight of water.

Water vapor in the air is called **humidity**. The humidity of our houses in winter is very low, and the measures usually adopted to moisten the air are ineffective. The higher the temperature of the house, the drier the air becomes, since its capacity for water is increased but no water vapor is added to it.

Distillation is the process of converting water into steam, condensing the steam by cooling, and collecting the pure water formed in a separate vessel. The mineral impurities remain in the vessel in which the water was boiled. Rain water is natural distilled water, but it is less pure than the artificial product.

The *freezing point* of water under a pressure of 1 atmosphere is the zero of the centigrade scale, and the *boiling point* is called 100° . Solutions of solids freeze at a lower temperature and boil at a higher temperature than pure water.

The **calorie** (small) is the amount of heat required to raise the temperature of 1 gram of water 1° C.

The **Calorie** (large) is the amount of heat required to raise the temperature of 1 kg. of water 1° C.

The **British thermal unit** (B.t.u.) is the amount of heat required to raise the temperature of 1 lb. of water 1° F.

Boiling is a good method of sterilizing a suspected water in the household. On a large scale, sterilization with ozone and with chlorine are in successful use. Most American cities purify their water supplies either by slow sand filtration or by rapid sand filtration.

EXERCISES

1. Compare the formation of rain with the process of distillation.
2. What are the chief functions of the water in the soil? What is "dry farming"?
3. Is it correct to say that damp air is *heavy*? Why should a fire burn badly on a rainy day?
4. What are the most important units of heat in use by engineers?
5. Explain the chief differences between slow and rapid sand filtration.
6. Does passing water through a Pasteur filter make the water suitable for chemical purposes? Explain.
7. If given a sample of perfectly clean water, how would you proceed to determine whether it had been distilled or not?

8. Devise a method of determining the total amount of solid matter contained in a sample of ordinary well water.

9. How could you prove that the common fruits and vegetables contain water? How could the percentage of water in them be determined?

10. How can sea water be made drinkable? What becomes of the salt when this is done?

11. Does distillation occur in nature? Explain.

12. It is a common belief that water vapor is *heavier* than air. If this were true, where would the formation of clouds take place?

13. Would it be safe to use for cooling beverages ice that had been cut from a polluted stream?

14. What is the source of the water supply of your home? How is it purified? Or is it merely *sterilized*?

15. How could you ascertain whether a sample of colorless liquid were water or not?

16. In what way does water aid in keeping the temperature of the body constant?

17. What property of water fits it especially for use as the cooling fluid in automobile radiators?

REVIEW QUESTIONS

1. Give three proofs that water contains hydrogen.

2. How could you detect oxygen in water?

CHAPTER IX

SOLUTION

80. Potassium chlorate solution. Potassium chlorate *dissolves* in water. This means that when stirred with water it disappears, leaving the liquid clear. The same thing happens when potassium chlorate is merely covered with water and left to itself, though a much longer time is required. It gradually *diffuses* through the water, and the final result is a uniform mixture of the molecules of both.

A solid that behaves in this way is said to be **soluble** in water. The corresponding negative word is **insoluble**. The product obtained is called a **solution**; in it the liquid, which in this case is water, is called the **solvent**, and the solid which has mingled its molecules with those of the solvent is termed the **solute**.

An insoluble solid, like clay, can be dispersed through water by shaking, but the mixture will be *turbid*, like muddy water. A turbid mixture of a solid and a liquid is called a **suspension**. Under certain conditions oil can be disseminated in microscopic drops through water, forming a liquid which looks like milk and which is largely used as a lubricant in cutting steel. Such a mixture of two liquids is called an **emulsion**. In time suspended matter will separate by gravity, leaving the liquid clear. Dissolved matter never separates in this way. The most important distinctions between solutions and suspensions are summed up in the following table:

By slowly adding potassium chlorate to a definite quantity of water it can be shown that there is a limit to the amount that the water will dissolve. One hundred grams of water at the freezing point will take up 3 grams of potassium chlorate,

and no more. The solution is then **saturated**, and any additional potassium chlorate thrown into it will merely fall to the bottom and form a layer which, no matter how thick, does not increase the proportion dissolved.

DISTINCTIONS BETWEEN SOLUTIONS AND SUSPENSIONS

Distinction in	Suspension	Solution
1. FORMATION	Made by some external action, such as shaking the solid with the liquid	Hastened by shaking, but also formed <i>spontaneously</i> from solid and liquid in contact
2. APPEARANCE	Turbid	Clear
3. "KEEPING" QUALITIES	Solid separates	Permanent
4. EFFECT OF FILTERING	Solid retained by filter	Unchanged
5. QUANTITY OF SOLID TAKEN UP BY 100 C.C. OF WATER	No definite limit	Definite amount at each temperature
6. FREEZING POINT	0°, same as pure water	Always below 0°
7. BOILING POINT	100°, same as pure water	Always above 100°

81. Effect of temperature. By making similar experiments at various temperatures it has been proved that the amount of potassium chlorate taken up by 100 grams of water increases rapidly with rising temperature. At room temperature (20° C.) the solubility is more than twice that at zero, while at 100° C. the quantity dissolved is 8 times as great as at room temperature.

Results of this kind are most readily pictured by a "curve." In Figure 55 the distances measured from left to right indicate

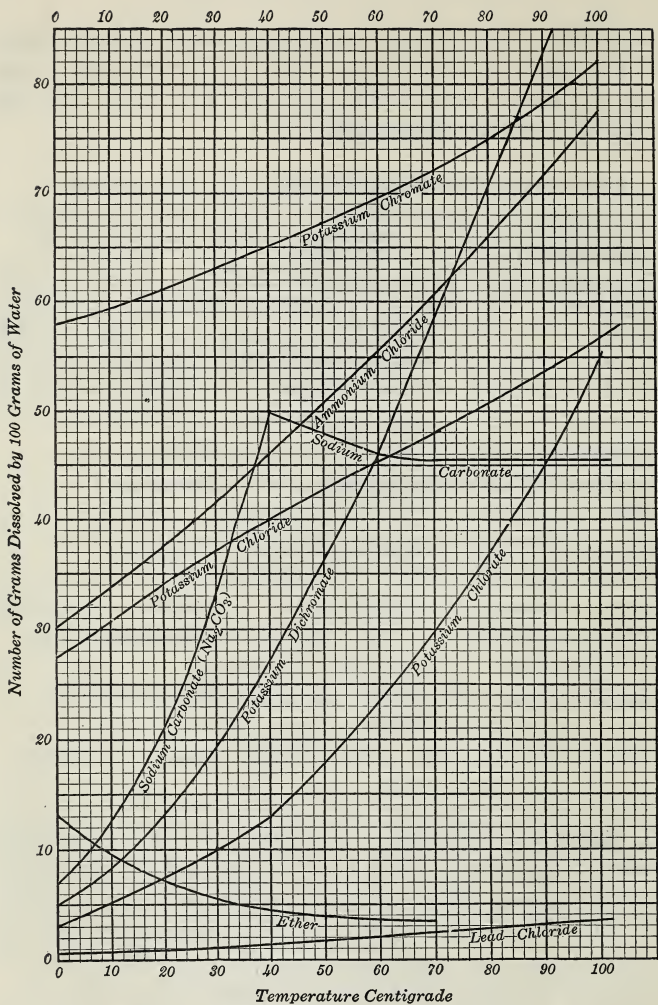


Fig. 55. Temperature-solubility curves of typical substances.

temperatures, and the distances upward, grams of the solid dissolved by 100 grams of water. The ascent of the curve for potassium chlorate shows the regular increase in its solubility with rising temperature. Further inspection of Figure 55 shows that most of the curves resemble that for potassium chlorate. It is a fact that almost all solids are more soluble in hot water than in cold. Slaked lime, gypsum, and a few other solids, however, *decrease* in solubility when the temperature rises. This can be illustrated by boiling a little limewater, which at once becomes turbid from the separation of some of the lime. Increase of *pressure* has little effect on the solubility of a solid.

The same solid usually behaves quite differently in different liquids. Thus, potassium chlorate is almost insoluble in alcohol. Rosin and shellac, which are unaffected by water, dissolve freely in alcohol, a fact which is applied in the manufacture of varnish. The "spirits" and "tinctures" of the druggist are solutions in alcohol, and most of them contain substances that in water dissolve slightly, if at all. Oils and fats are insoluble in water but readily soluble in gasoline. Hence the use of gasoline for cleansing clothing; the foreign material that collects on garments is held in an oily film and falls off when this cement is dissolved away.

82. Colloidal solutions. Let us consider the properties of a liquid through which a powder of *gold* is disseminated. When the particles of gold are fairly large—4 microns in diameter or thereabouts, the turbid liquid is a true suspension, which soon settles, and under the microscope no vibratory movement of the particles can be perceived. But when the particles are very small—about 0.01 micron in diameter—the gold does not settle even if the preparation is kept for years. The liquid is red in color and is quite clear both to the naked eye and under the microscope. Particles so small are beyond the power of the microscope and must be sought for with the *ultra-microscope*, a simple form of which is shown in Figure 56. A beam

of sunlight reflected from a mirror S into a darkened room is focussed by a lens L into the liquid, which is contained in a little glass trough b . The liquid is examined with a powerful microscope, the field of which is *dark* because the rays of light pass by at right angles; the only light that enters the tube is that which is bent out of its course by the gold particles. They appear, therefore, bright against a dark ground, like stars in the sky, and, like stars, they seem mere points, without any visible

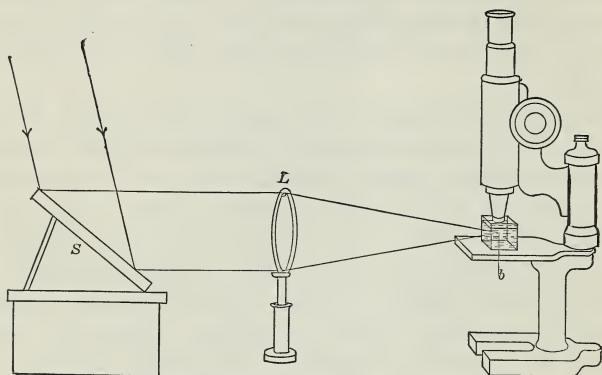


Fig. 56. A simple form of ultra-microscope.

diameter. With this instrument the liquid is seen to be filled with multitudes of red, yellow, and green particles, all of which are in ceaseless, rapid, zig-zag motion, which continues, no matter how long the preparation is preserved. Except for the colors, the appearance is similar to that of a swarm of gnats flying about in a sunbeam. The motion is shown, enlarged 3,000 diameters, in 1 of Figure 57, while 2 and 3 in the same figure represent the movement of particles of larger diameter. From the discussion in Chapter VI the student will perceive that we are here again confronted with the *heat motion of the molecules*, which affects the gold particles because they are so extremely small. Their movement not only resembles in

general character that assumed by the molecular theory, but actual measurements show that the speed of a particle and the average distance it travels in a straight line before changing

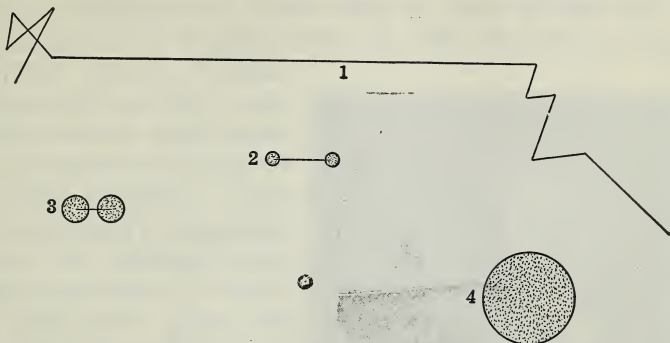


Fig. 57. Motions of particles in a colloidal solution of gold, enlarged 3,000 diameters.

Diameters of particles: 1, 0.00001 mm.; 2, 0.0005 mm.; 3, 0.001 mm.; 4, 0.004 mm. (motionless).

its direction are equal to the values obtained by calculation from the theory.

A liquid of this kind, which stands on the boundary between solution and suspension, is called a **colloidal solution**. A simple method of making a colloidal solution of gold is shown in Figure 58. Two rods of gold, connected with a dynamo circuit of 220 volts, are brought close together under the surface of distilled water. An electric arc burns between the two rods with a rattling noise, and a reddish color rises from them and fills the liquid. The gold is vaporized by the heat of the arc, and the vapor is condensed so suddenly by the cold water that there is no time for the molecules to arrange themselves into crystals. Particles containing

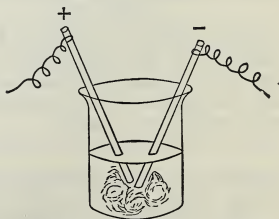


Fig. 58. Making a colloidal solution of gold.

only a few molecules are formed, and these form a colloidal solution in the water. Silver, copper, platinum, and some other metals can be used instead of gold with similar results.

By various means a great variety of substances can be dispersed through water and other liquids in this condition of

nearly molecular subdivision. Mucilage, liquid glue, starch paste, and raw white of egg are colloidal solutions. Colloidal solutions containing a large quantity of the dispersed solid often "set" to a semi-solid mass on cooling. The jellies of the household are in this condition. Soap forms a colloidal solution with water, and its remarkable cleansing power is due mainly to its ability to induce films of grease and other foreign matter to follow its example and enter into colloidal solution in water. Our food passes into colloidal solution during digestion. Colloidal solutions play a most im-

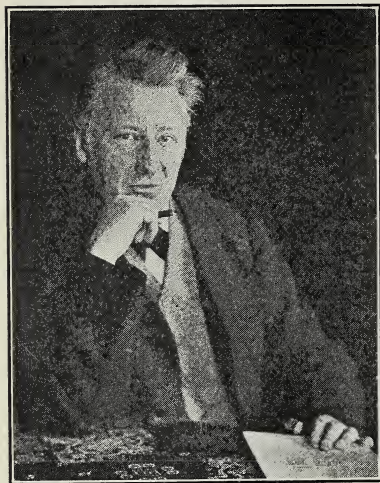


FIG. 59. JACOBUS HENDRICUS VAN'T HOFF (1852-1911).

Dutch chemist, professor of physical chemistry in the University of Berlin; founded the modern theory of solution and investigated the arrangement of atoms within the molecule.

important part in the life processes of animals and plants.

83. Solutions of gases in liquids. All gases are soluble in water, but the differences in degree of solubility are very great. Thus, 100 c.c. of water at 0°C . dissolves 2 c.c. of hydrogen, a gas the solubility of which is small, whereas 100 c.c. of water at 0°C . dissolves 129,800 c.c. of ammonia, which is one of the most soluble gases. The higher the temperature, the *less* the

solubility of a gas in a liquid; 100 c.c. of water at room temperature dissolves only 70,000 c.c. of ammonia, and boiling water dissolves none. Most gases can be almost completely expelled from their solutions by boiling the liquid, though there are some to which this statement does not apply. The insipid flavor of boiled water is due to the removal of the dissolved gases during the process of sterilization by boiling.

Pressure increases the solubility of gases. With gases the solubility of which is not large, the weight of the gas dissolved by the liquid is *proportional* to the pressure. Soda water is water into which carbon dioxide gas has been forced under a pressure of about 3 atmospheres. The water dissolves about three times as much of the gas by weight as it would at ordinary pressure. When the liquid issues into the air, the pressure is removed and the additional gas escapes in bubbles. The term **effervescence** is applied to this behavior. The effervescence of many beverages when the bottles are opened, and of mineral waters when they escape from the rocks, is due to the liberation of dissolved carbon dioxide as gas when the pressure is reduced.

84. Solutions of liquids in liquids. A little ether added to water dissolves, but more ether forms a layer at the top. This upper layer is rich in ether and poor in water; in it the ether is *solvent* and the water is *solute*. The lower layer contains far more water than it does ether; here the water is *solvent* and the ether *solute* in it.

A liquid like kerosene, which seems to separate at once when only a drop of it is added to water, really acts like ether. The water dissolves some kerosene and the kerosene some water, but the solubilities are small, and it requires careful work to detect a trace of either liquid in the other.

Alcohol and water can be mixed in any proportion whatever without separation. The same statement is true of alcohol and ether and of some other pairs of liquids. All gases behave like alcohol and water—that is, they can be added to each

other in any proportions with formation of a homogeneous mixture.

85. Solid solutions. The fact that spongy platinum absorbs a hundred times its volume of hydrogen has already been mentioned. The product is a **solid solution**, similar to the solution of the same gas in water except that the solvent is solid and the volume of gas taken up is 5,000 times as great. Oxygen forms a solid solution with rubber; the gas remaining in a tire that has stood for some time without being pumped up is mostly nitrogen, for the oxygen has been absorbed. Colored cloth is, in many cases, a solid solution of the dye in the fabric. Many kinds of candy are made by melting the sugar, dissolving the other ingredients in the liquid, and letting the mass cool to a solid solution. Ruby glass is a solid colloidal solution of gold in glass.

Even *diffusion* may occur, though very slowly, in a solid solution. One end of a lead cylinder was polished to a plane surface, as nearly perfect as possible, and laid upon a gold disc which had been treated in the same way. The two were placed in a bank vault, where there was no vibration and where the temperature was practically constant, and were left undisturbed. Molecules of gold slowly travelled into the lead, and after some time gold could be detected several centimeters from the junction.

Hence there is no reason for restricting solution to liquids. Solid, liquid, or gas may act as solvent or as solute. But liquid solutions are easiest to make and to handle and are by far the most important.

86. Supersaturated solutions. When a solution that has been saturated while hot is allowed to cool, the excess of the solute, above the quantity that the water will dissolve in the cold, usually deposits in crystals. There are, however, some solutions that, when treated in this way, remain without crystallizing, forming what is called a **supersaturated solution**. This contains more of the solute than does the saturated

solution. The excess of solute in a supersaturated solution may crystallize at any time, especially if the liquid is shaken. It will always crystallize at once if a fragment of the solute is dropped into it.

The saturated solution is the most concentrated that can be obtained by shaking the solid with the liquid. The supersaturated solution is more concentrated than the saturated, but it can only exist in the absence of the solid, the excess of which tends to separate.

87. Water of crystallization. When alum is heated gently in a test tube, the transparent crystals yield a white mass called "burnt alum," and drops of water condense in the cooler part of the tube. The colorless, glassy crystals of washing soda act in the same way, giving off nearly two-thirds of their weight of water and leaving a white powder of dry soda.

This water which forms part of the crystals deposited from aqueous solutions is called **water of crystallization**. It is chemically combined with the solute, for the water does not betray its presence by any dampness of the crystal, and there is a complete change of properties when the crystal is heated, two new substances, the dry solid and water, being formed. Moreover, crystals of the same substance always contains the same percentage of water, which, according to the law of definite proportions, is the chief characteristic of a chemical compound.

Some substances when deposited from aqueous solution form crystals which contain no water. Among these may be mentioned sugar, salt, and potassium chlorate. To such crystals the term *anhydrous*, which means free from water, is applied.

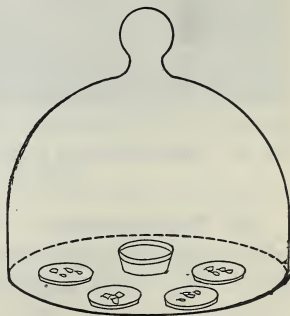
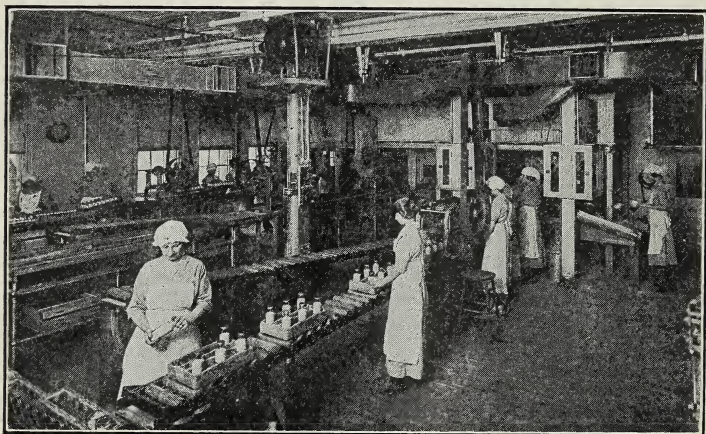


Fig. 60. Apparatus for investigating efflorescence and deliquescence.

88. Efflorescence. Crystalline washing soda when kept allows its water of crystallization to escape as vapor into the air and falls to a white powder. This loss of water of crystallization is called **efflorescence**. Some crystals containing water effloresce, but others are permanent. The lower the humidity, the greater the tendency to efflorescence.



Courtesy of the Carrier Engineering Corporation.

Fig. 61. Installation for supplying artificially dehumidified air to a packing room for deliquescent chemicals.

89. Deliquescence. When sodium hydroxide is exposed to air, it absorbs water, becomes damp, and finally forms a solution. The term **deliquescence** is applied to this behavior, which is also met with in many other substances. *Calcium chloride*, which is an inexpensive deliquescent substance, is often placed upon roads to keep them damp and to prevent dust, which it does by absorbing water from the air.

The higher the humidity, the greater the tendency to deliquescence. Salt and sugar remain dry in an ordinary climate, but at the seashore their deliquescence is noticeable and troublesome, because there the humidity is often nearly

100 per cent. Air saturated with moisture is easily obtained by merely placing a dish of water under a bell jar (Fig. 60). In such an atmosphere all soluble solids will be found to deliquesce. The same apparatus can be used for experiments upon efflorescence by replacing the water by sulphuric acid, which removes the water from the air in the bell jar and reduces the humidity to practically zero. Many crystals that are permanent in ordinary air effloresce rapidly in air artificially dried in this way.

SUMMARY

A solution is **saturated** by shaking it with the solute until it will take up no more.

When a hot saturated solution is cooled in the absence of the solute, a **supersaturated** solution may result. This deposits crystals when a fragment of the solute is dropped into it.

The solubility of most solids increases with rising temperature.

The solubility of gases decreases rapidly as the temperature rises.

In a true **solution** the solid is divided into its molecules, which mingle uniformly with those of the liquid.

A **suspension** contains coarse particles each of which is composed of innumerable molecules.

Colloidal solutions lie between solutions and suspensions. The subdivision of the solute is excessively fine but not quite molecular.

Water chemically combined in crystals is called **water of crystallization**. The water is present in definite proportions, and, when it is driven out by heating, a complete change in properties results.

Efflorescence is the gradual escape of water of crystallization at ordinary temperatures.

Deliquescence is the slow absorption of water from the air with the formation of a saturated solution.

EXERCISES

1. Explain the meaning of a solubility curve.
2. Distinguish between *saturated* and *supersaturated* solution.
3. When ether is added to water, which liquid is solvent and which solute in the upper layer? In the lower layer?
4. Mention some familiar colloidal solutions.
5. What is the difference between a colloidal solution and a true solution? Between a colloidal solution and a suspension.
6. Give some well known examples of solid solutions.
7. Prove that water of crystallization is chemically combined with the solute.
8. How can the connection of water vapor with deliquescence and efflorescence be investigated experimentally?
9. If washing soda that had effloresced could be bought at the same price as the clear crystals, would it be an advantageous purchase?
10. The sirups of the household often deposit crystals of sugar, although neither cooling nor evaporation has occurred. Explain this fact.
11. Why does sea water freeze less readily than river water? How would the freezing point of water from the Great Salt Lake compare with that of sea water?
12. What is the difference between the effect of water on sugar and the effect of sulphuric acid on zinc?
13. If potatoes were boiled in a saturated solution of salt, would they cook more or less rapidly than in pure water?
14. Explain the effervescence of ginger ale, soda water, and some spring waters.
15. Why is salt added to the ice in freezing ice cream? Could any substance other than salt be used with the ice?
16. How could you find out whether a given solution was saturated, unsaturated, or supersaturated?
17. How could you ascertain whether a solution was colloidal or not?

18. Is a solution a chemical compound of the solute with the solvent?

19. 10.98 grams of a solution of potassium chlorate were placed in a weighed dish and evaporated to dryness. The solid that remained weighed 0.7025 gram. The solution had been saturated at 18° . Calculate how many grams of potassium chlorate were contained in 100 grams of the liquid.

20. Using the same figures, calculate how many grams of potassium chlorate will dissolve in 100 grams of *water* (not solution) at 18° .

21. Using the same figures, calculate how many grams of water at 18° are needed to dissolve 1 gram of potassium chlorate.

22. A solution of table salt saturated at 15° contained 26.39 per cent of salt. How many grams of salt will 100 grams of water dissolve at 15° ?

CHAPTER X

COMPOSITION OF WATER; HYDROGEN PEROXIDE; THE LAW OF MULTIPLE PROPORTIONS

90. The composition of water. Let us recall the facts bearing upon the composition of water that are already available to us. The behavior of zinc with steam has shown us that the latter is composed of hydrogen and oxygen, a conclusion which, as we have seen, is corroborated by burning hydrogen in oxygen and thus producing water. Further confirmation is found in the action of hydrogen upon heated oxides of metals, whereby it removes the oxygen, forming water with it, and liberates the metal (§ 69). A study of the interaction of sodium with

water (§ 64) has indicated that the hydrogen of the water can be separated into two equal portions, one of which escapes, while the other remains combined with the sodium and the oxygen. By means of the electric current we have analyzed water into its constituents (§ 65) and have found that 2 volumes of hydrogen and 1 volume of oxygen are liberated.

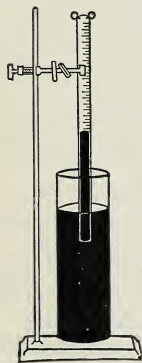


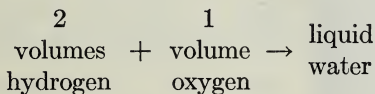
Fig. 62. Synthesis of water in the eudiometer.

91. Synthesis of water by volume. Let us now investigate the *synthesis* of water, that is, the preparation of the compound from its elements. The graduated tube in Figure 62 is called a *eudiometer*. It is filled with mercury and inverted in a narrow cylinder containing the same liquid. Hydrogen and oxygen are introduced and are made to combine with a slight

explosion by passing an electric spark between the two platinum wires which pierce the glass near the upper end of the apparatus.

When exactly 2 volumes of hydrogen and 1 of oxygen are taken, the gases combine completely, forming a film of moisture on the glass, and the mercury fills the tube with such energy that breakage is quite likely. It is better, therefore, to take an excess of one of the gases, so that after the explosion some gas will remain to arrest the mercury before it reaches the top of the tube.

Suppose that 10 c.c. of each gas is used. Then after the explosion 5 c.c. of gas will be found in the tube, which the spark test will show to be *oxygen*. Thus, 10 c.c. of hydrogen have united with 5 c.c. of oxygen, or,



92. Volume of the steam produced.

In the experiment just described the combination of the hydrogen and the oxygen first forms *steam*, which is at once condensed by the cold walls of the measuring tube. If the tube be kept hot, the steam will *not* condense, and its volume can be measured and compared with that of each of the gases that united to form it. The apparatus is shown in Figure 63. The heating device consists of a wide glass tube surrounding the tube in which the gas is measured. Through it is passed the vapor of some liquid that boils above 100°. *Amyl alcohol*, commonly called fusel oil, is a suitable liquid for this purpose. It boils at a somewhat higher temperature than water. It is impossible,

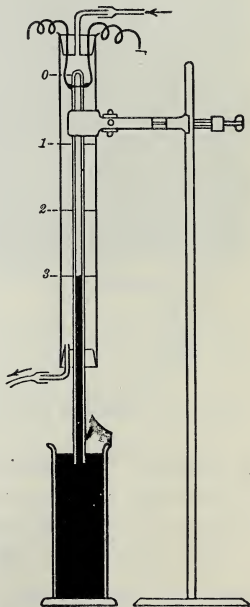


Fig. 63. Measuring the volume of steam produced by the union of hydrogen and oxygen.

therefore, for the steam to condense so long as the tube surrounding the eudiometer is kept filled with amyl-alcohol vapor.

In this experiment it is unnecessary to use an excess of oxygen, for the steam will prevent the mercury from striking the top of the graduated limb. We may take, therefore, 10 c.c. of hydrogen and 5 c.c. of oxygen. After the explosion the volume of the steam is found to be 10 c.c., *equal to that of the hydrogen*. Hence:

2 volumes hydrogen + 1 volume oxygen $\rightarrow$ 2 volumes steam

93. Composition of water by weight. From the composition of water by volume its composition by weight can easily

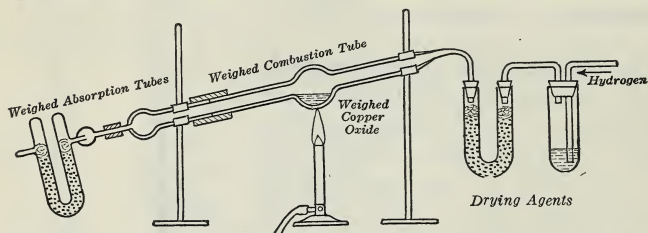


Fig. 64. Apparatus for determining the composition of water by weight.

be deduced. In round numbers oxygen is 16 times as heavy for the same volume as hydrogen, so that by weight water must contain 2 parts of hydrogen to 16 of oxygen.

This calculation can be confirmed by passing dry hydrogen over hot copper oxide in a weighed glass tube. The copper oxide is changed to copper, with loss in weight due to the loss of oxygen, which has combined with hydrogen to form water. Figure 64 is a diagram of the apparatus. Hydrogen from a Kipp generator passes from right to left as the arrow indicates. The first two tubes contain drying agents to remove the water vapor from the gas. Then follows the

heated tube in which the reduction of the copper oxide takes place. Most of the water formed condenses in the bulb that follows the hot tube, and the last traces are absorbed in the U-tube at the extreme left, which contains drying agents and which is weighed with the bulb before and after the experiment. The gain in weight here is the weight of the water formed. The weight of the hydrogen in this water is obtained by subtracting the weight of the oxygen lost by the copper oxide from the weight of the water.

The results corroborate the calculation of the composition of water from the synthesis by volume. Water, therefore, contains two-eighteenths, or one-ninth, of its weight of hydrogen, and sixteen-eighteenths, or eight-ninths, of its weight of oxygen.

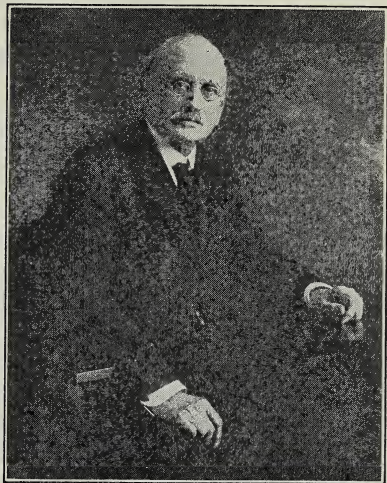


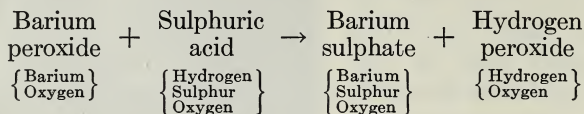
FIG. 65. EDWARD WILLIAMS MORLEY
(1838-).

American chemist, professor of chemistry in Western Reserve University; determined the exact ratio in which hydrogen and oxygen combine by weight.

HYDROGEN PEROXIDE

A second compound of hydrogen and oxygen has been obtained, containing twice the weight of oxygen combined with the same weight of hydrogen as does water. Whereas water contains by weight 2 parts of hydrogen and 16 parts of oxygen, **hydrogen peroxide** contains 2 parts of hydrogen and 32 parts of oxygen by weight.

94. Preparation and properties. Hydrogen peroxide is made from *barium peroxide*, a white powder which is an oxide of barium, a metal similar to calcium. The barium peroxide is stirred up with water, and the creamy liquid added to a cold dilute solution of sulphuric and phosphoric acids in water:



The white, insoluble solid matter which is formed is composed of barium sulphate with some barium phosphate. After it is allowed to settle, the clear solution of hydrogen peroxide is siphoned off and bottled.

Pure hydrogen peroxide is a colorless sirup. It is nearly $1\frac{1}{2}$ times as dense as water, with which it mixes in all proportions. It is a dangerous substance, tending to separate into water and oxygen with explosive violence.

Commercial hydrogen peroxide is a 3 per cent solution in water. It is non-explosive, although it slowly gives off oxygen. For this reason the cork of the bottle is often wired in. The escape of the oxygen occurs at once when certain catalysts, such as finely divided platinum, gold, silver, or manganese dioxide, are added. The commercial hydrogen peroxide yields 10 times its volume of oxygen; for this reason it is called "10-volume solution."

95. Uses. Owing to its readiness to give up oxygen, hydrogen peroxide is a strong *oxidizing agent*. This explains its use in bleaching hair, wool, silk, feathers, and ivory, of which it oxidizes and destroys the coloring matters. It assists in restoring the original colors to oil paintings that have become dark with age. It is valuable in the household for disinfecting cuts and other minor wounds.

From the way in which it is made, commercial hydrogen peroxide often contains a little sulphuric acid. Because of

this, when it is to be used in treating the throat, limewater should be mixed with it to neutralize the sulphuric acid and prevent irritation of the mucous membrane.

THE LAW OF MULTIPLE PROPORTIONS

96. Water contains by weight 2 parts of hydrogen and 16 parts of oxygen. Hydrogen peroxide contains by weight 2 parts of hydrogen combined with 32 parts of oxygen. Taking a definite weight of hydrogen as a basis, the weight of oxygen in water bears to the weight of oxygen in hydrogen peroxide the relation of 1 to 2.

There are many other pairs of elements that unite with each other to form two or more compounds. In all such cases, if we consider a fixed weight of one element, the quantities of the other element combined with that weight in the two compounds bear a simple relation to each other. A simple relation means a ratio that can be expressed by small whole numbers, for example, 1 : 2, 1 : 3, or 2 : 3.

This fact, which was discovered by John Dalton, is called the **law of multiple proportions**. It may be expressed as follows:

Let A and B be two elements that form two compounds with each other. Then the weights of B that combine with a fixed

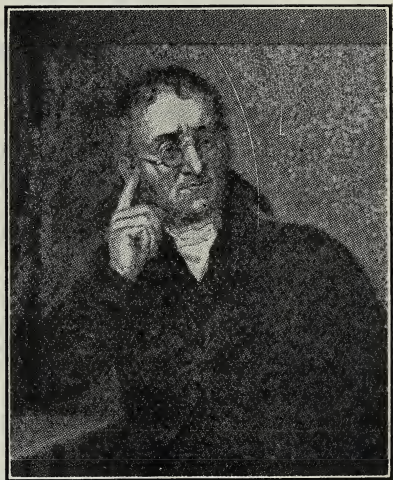


FIG. 66. JOHN DALTON (1766–1844).

English schoolmaster and chemist; discovered the law of multiple proportions and advanced the atomic theory.

weight of A in the two compounds stand in a simple numerical relation to each other.

If there are more than two compounds of the same two elements, the law still holds good. The five compounds of nitrogen and oxygen furnish a remarkable case of multiple proportions. In the following table the name of the compound is in the first column. In the second, the fixed weight of nitrogen which serves as a basis is stated. The third contains the different weights of oxygen that are found to be combined with this weight of nitrogen in the five compounds. The figures in the last column are obtained by dividing those of the third by 16, the number of parts of oxygen by weight in nitrous oxide.

MULTIPLE PROPORTIONS IN THE FIVE OXIDES OF NITROGEN

Name	Nitrogen	Oxygen	Ratio
Nitrous oxide.....	28	16	1
Nitric oxide.....	28	32	2
Nitrogen trioxide.....	28	48	3
Nitrogen peroxide.....	28	64	4
Nitrogen pentoxide.....	28	80	5

SUMMARY

The **synthesis** of water by volume agrees with the conclusion from electrolysis, that water contains 2 volumes of hydrogen and 1 volume of oxygen. When the steam formed by the combination is not allowed to condense, its volume is found to be equal to that of the hydrogen.

Calculation from the composition by volume shows that water must contain by **weight** 1 part of hydrogen and 8 parts of oxygen. Direct experiment by weight confirms this result.

Hydrogen peroxide is made by adding barium peroxide to a cold mixture of dilute sulphuric and phosphoric acids. It is a

strong oxidizing agent and is used for bleaching and as a disinfectant.

The **law of multiple proportions** can be formulated as follows:

Let A and B be two elements that form two compounds with each other. Consider a fixed weight of A. Then the weights of B combined with this weight of A in the two compounds are in the ratio of small whole numbers.

EXERCISES

1. Steam contains its own volume of hydrogen and in addition half its volume of oxygen. Has this any bearing upon the theory of the existence of molecules? Many similar cases are known. Would it be possible to explain them upon the supposition that matter was continuous?

2. Summarize briefly all the evidence at hand for the composition of water.

3. Explain the law of multiple proportions, using water and hydrogen peroxide as examples.

4. 20 c.c. of hydrogen and 20 c.c. of oxygen are mixed in a eudiometer and the mixture exploded. How many cubic centimeters of water vapor are formed? Which gas remains in excess, and how many cubic centimeters of it?

5. A mixture of 20 c.c. of hydrogen with 6 c.c. of oxygen is exploded in a eudiometer. (a) How many cubic centimeters of water vapor are produced? (b) Which gas remains in excess and how many cubic centimeters of it?

6. The weight of a liter of oxygen is 1.43 grams, and that of a liter of hydrogen is 0.09 gram. Calculate the composition of water in parts by weight from the results of the electrolysis of water.

7. Hydrogen was passed over copper oxide. The loss in weight of the copper oxide was 808.640 grams. The water produced weighed 909.720 grams. Required, the composition of water in *parts by weight*.

8. A current of steam is passed over heated zinc until the increase in weight of the zinc is 8 grams. (a) What is the weight of the hydrogen produced? (b) How many liters of hydrogen are formed? (Refer to 6 above.)

9. Compare the properties of water with those of hydrogen peroxide.

10. Explain the statement that bleaching by hydrogen peroxide is oxidation.

11. Water contains nearly four times as much oxygen by weight as does air, and yet water *extinguishes* fire. Why?

12. What would be the proper chemical name of water?

CHAPTER XI

THE ATOMS

97. The nature of the molecules. The study of the physical properties of gases and the examination of colloidal solutions in the ultra-microscope lead us necessarily to the conviction that substances are composed of molecules. The idea that matter is built up of particles was stated with great precision by *Democritus*, the greatest philosopher of antiquity, who lived in Greece five centuries before the beginning of the Christian Era. Democritus, basing his theory upon the limited knowledge available at that time, regarded the particles as little spheres, without structure, infinitely hard and therefore incapable of wear or of any kind of subdivision. Let us examine this view in the light of some of the facts already studied.

98. The molecule of water. Any quantity of pure water is composed of water molecules, all of which are exactly alike. Hence, one molecule would be a perfect sample of the whole. If we could catch a single molecule and analyze it, the results would apply rigorously to an ocean of water, provided only that the water were *pure*, that is, that no other molecules were mixed with the water molecules in it.

Moreover, the two elements that are obtained by analyzing weighable quantities of water must be contained in each individual water molecule. Every water molecule must contain oxygen and hydrogen, and the hydrogen must be in two separate portions, equal in weight, one of which can be removed by the action of sodium without disturbing the other.

99. Atoms. Only one interpretation of these facts is possible. The water molecule is composed of smaller particles. There are in it at least 1 oxygen particle and 2 hydrogen

particles. These are called **atoms**. Similar reasoning applies to other chemical compounds. *The atoms of the elements are the smaller particles of which the molecules of substances are composed.* There can be no such thing as an atom of water or of any other chemical compound; *only the elements exist as atoms.* Since about eighty elements are known, there are about eighty different kinds of known atoms, which, by combining with each other in an endless variety of ways, yield the 200,000 or more substances which are at present known to the chemist. Chemists are daily grouping the atoms in new ways and forming molecules unknown before, each of which means the production of a new substance, but they are unable to bring about the formation of new atoms, nor, as we have seen, can they transform one atom into another of a different species.

100. Atomic weights. We have noted that the symbol of an element indicates a definite quantity by weight in which the element is found to be present in all of its compounds; these weights are given in a table in the Appendix to this book. Every oxygen compound contains 16 parts of oxygen by weight or some small multiple of that quantity. Every compound of sulphur contains the weight of sulphur denoted by the symbols, 32 parts, or some quantity that can be obtained by multiplying 32 by a small whole number.

The weights indicated by the symbols are the *relative weights of the atoms of the elements*, that of oxygen being taken as equal to 16, which is almost the same as setting hydrogen equal to 1.

Several different methods of experiment have shown us that water contains by weight 2 parts of hydrogen and 16 parts of oxygen. If the atomic weight of hydrogen is 1 and that of oxygen is 16, the water molecule must contain 2 atoms of hydrogen and 1 atom of oxygen. Representing an oxygen atom by a large white circle and a hydrogen atom by a smaller black circle, we may picture the water molecule thus: •○•

The method of representing molecules employed by chemists is to place together the symbols of the elements, each of which

represents an atom. When more than one atom of the same element is present in the molecule, the symbol is multiplied by the proper number by means of a small numeral placed just below the middle of the symbol and to the right. Thus, the expression for the molecule of water becomes H_2O , which is called the **formula** of water, and which, as will be seen, is a complete statement of its composition. Similar formulas are used for the molecules of all other compounds.

101. Definite and multiple proportions. The *law of definite proportions*, which states that the composition of a chemical compound does not vary, can now receive a simple explanation. All water molecules contain 2 atoms of hydrogen, each of which weighs 1, and 1 atom of oxygen, which weighs 16. Hence the composition of pure water must be always the same. It must contain one-ninth of its weight (11.1 per cent) of hydrogen and eight-ninths of its weight (88.9 per cent) of oxygen. The law of definite proportions, then, depends upon the facts that the molecules of the same compound are always composed of the same atoms, and that each of these atoms has a definite weight.

If, starting with water, we desire to make another compound also containing 2 atoms of hydrogen but richer in oxygen, the only possibility is to introduce, directly or indirectly, another atom of oxygen into the molecule H_2O . This gives the molecule H_2O_2 , which is, in fact, the formula of *hydrogen peroxide*. But in adding a second atom of oxygen we have evidently doubled the weight of oxygen combined with the 2 parts of hydrogen. It is evident that any compound standing between water and hydrogen peroxide in oxygen content is impossible. Hence the *law of multiple proportions*.

102. Physical and chemical changes. Now that we have studied the structure of matter, we can return to the subject of physical and chemical changes and draw a more precise distinction between them. In ice, as in all crystalline solids, the location of each molecule is fixed, and its motion is a vibration

to which definite limits are set. When ice melts, these limits are abolished, and the molecules are set free to journey wherever their chance encounters may send them in the liquid. If the water is in turn converted into steam, the molecules move much farther apart, and the distance through which a molecule moves between two encounters is correspondingly increased. These alterations bring about great changes in the *physical* properties, so that liquid water is very different from ice and steam from both, yet the molecule remains the same. It is still composed of 2 atoms of hydrogen in union with 1 of oxygen, and the group of 3, like all molecules, moves as a unit without separation in the heat motion of the solid, the liquid, and the gas.

A physical change may affect the motion or the arrangement of the molecules, but not the nature of the molecules themselves.

On the other hand, in the electrolysis of water the molecule H_2O is torn apart, the hydrogen is liberated at one electrode and the oxygen at the other. This is a *chemical* change. Evidently the distinction is that it alters the molecule itself, which a physical change does not.

A chemical change breaks up existing molecules and forms new ones from them.

Both physical and chemical changes leave the *atoms* unaffected. We shall see later that in the changes that occur in radium and other radioactive elements the atoms themselves disintegrate, but this point must be reserved for future study.

SUMMARY

Molecules are composed of smaller particles called **atoms**. The atoms of the same element are alike. Since there are about 80 different known elements, there are about 80 different kinds of atoms.

The **symbol** of an element denotes its *atom*. The **atomic weight** is the weight of the atom, that of oxygen being assumed as 16, which makes the atomic weight of hydrogen about 1.

To represent the **molecule** of a compound the symbols of the atoms which it contains are placed together, multiplied when necessary by small figures placed after the symbols. The resulting expression is called the **formula** of the compound.

The atomic constitution of matter provides a simple explanation of the laws of definite and multiple proportions and a precise distinction between physical and chemical changes.

EXERCISES

1. What facts make it necessary to believe in the existence of smaller particles making up the molecules?
2. Explain exactly what is meant by the symbol H, the symbol O, and the formula H_2O .
3. Calculate the percentages of oxygen and hydrogen corresponding (a) to the formula H_2O , (b) to the formula H_2O_2 .
3. Distinguish between physical and chemical changes, from the molecular standpoint.
4. Explain how the law of definite proportions follows from the existence of atoms and molecules.
5. How many different kinds of atoms are there? Why?
6. How many different kinds of molecules are there? Why?
7. How does the molecule of a compound differ from that of an element?

REVIEW QUESTIONS

1. What is a *micron*? What is the diameter of the molecules of the air? How far are they apart?
2. What is the chief object in purifying public water supplies? Sketch two important methods of achieving this object.
3. If water were to cease sending vapor into the air, what changes would result upon the earth's surface?
4. Define the *calorie*, the *Calorie*, and the *British thermal unit*.
5. How could you at once convert a *supersaturated* solution into a *saturated* solution?
6. Explain the law of multiple proportions, using the compounds of nitrogen and oxygen as examples.

CHAPTER XII

CHLORINE

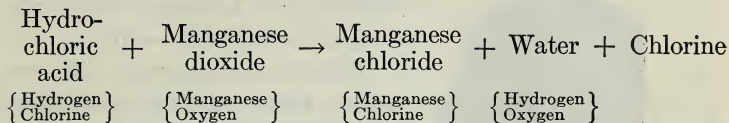
103. Common salt. The salt of the household is a compound of two elements, *sodium* and *chlorine*. Sodium is a metal which, if introduced into the mouth, would ignite from the moisture of the saliva, and chlorine is a suffocating, poisonous gas. The fact that two such elements unite to form a substance which is not only harmless, but necessary in the diet is a striking instance of the total change in properties that accompanies chemical combination.

104. Occurrence of chlorine. Chlorine is intensely active chemically and therefore does not occur native. *Active* elements tend strongly to enter chemical combination and usually do not remain in the free state in nature. Only one exception to this statement is sufficiently important to be noted, namely, oxygen. In that case the exception is due to the fact that oxygen is constantly being liberated by plants.

Sodium chloride, commonly called *salt*, is the most abundant chlorine compound. *Potassium chloride* occurs in large deposits in a few localities; like salt it is of great industrial importance. *Silver chloride* is utilized as an ore of silver but not as a source of chlorine.

105. Preparation. Chlorine is made on a large scale by the electrolysis of a solution of salt, a process which will be discussed later. In the laboratory *hydrochloric acid* is the starting point, and the chlorine is set free by oxidizing the hydrogen of the hydrochloric acid to water. This can be accomplished by means of the oxygen of the air, but it is more convenient to use an oxygen compound. The substance generally employed is *manganese dioxide*, with which we are already familiar (§ 26).

Manganese dioxide is a compound of a metal called *manganese* with oxygen. Only half of the chlorine of the hydrochloric acid is liberated by the action of the oxygen of the manganese dioxide; the rest combines with the manganese, forming *manganese chloride*:



Other substances rich in oxygen can be used instead of manganese dioxide. The apparatus is shown in Figure 67. Chlorine is too soluble in water to be collected over it. It is much heavier than air, and it is collected by allowing it to run into the bottom of a dry bottle, the air being forced out at the top. This is called collecting by *downward displacement*. The greenish-yellow color of the chlorine makes it easy to see when the bottle is filled, when it should be immediately replaced by another. The experiment should be carried out in a draft closet, and great care should be taken not to inhale the chlorine.

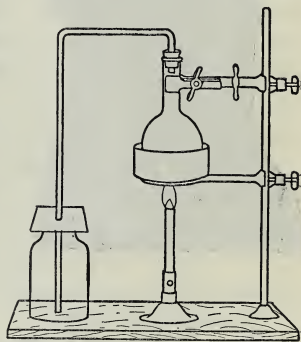


Fig. 67. Preparation of chlorine.

106. History. Chlorine was discovered by the Swedish chemist *Scheele*, who obtained it in 1774 by the method just described. On account of the mode of preparation it was at first supposed to be a compound of hydrochloric acid with oxygen. The English chemist Sir Humphry Davy in 1809 proved it to be an element.

107. Physical properties. Chlorine is greenish-yellow in color and suffocating in odor. It is $2\frac{1}{2}$ times as dense as air,

the weight of 1 liter being about 3.2 grams. Moderate pressure or cold converts it into a yellow liquid which boils at -34° .

Liquid chlorine is now an important article of commerce and is distributed in cylinders and in tank cars. Solid chlorine has been obtained by cooling the liquid to -102° .

Chlorine mixed with air produces, when inhaled, a condition of serious irritation of the respiratory passages, which is somewhat relieved by inhaling alcohol vapor or dilute ammonia. Inhalation of undiluted chlorine would at once be fatal.

Water at room temperature dissolves twice its volume of chlorine. Thus chlorine is far more soluble in water than oxygen or hydrogen but it does not approach the solubility of ammonia gas. The aqueous solution of chlorine, called *chlorine water*, is frequently employed in the laboratory as a substitute for the gas.

108. Chemical conduct. Chlorine is more active chemically than oxygen, especially at ordinary tem-

peratures. It converts all the *metals* into their chlorides, and the more active metals burn in the gas. Sodium when heated in chlorine takes fire and burns to salt with a dazzling yellow flame. Copper leaf ignites spontaneously in chlorine. Powdered antimony when dropped into the gas forms a shower of fire—a striking experiment. Inactive metals, like gold and platinum, unite more slowly with chlorine.



FIG. 68. KARL WILHELM SCHEELLE (1742–1786).

Swedish apothecary; discovered chlorine, manganese, barium, glycerin, and several other substances; first prepared potassium cyanide and proved that graphite is a form of carbon.

Among the *non-metallic elements*, arsenic behaves exactly like antimony; phosphorus ignites in chlorine and burns with a pale flame; sulphur, when heated, combines with the gas, forming a chloride which is an important commercial product. A flame of burning hydrogen becomes large and pale when immersed in chlorine. The colorless gas produced is *hydrogen chloride*, often called *hydrochloric acid*.

Chlorine has no action upon charcoal or upon any other form of carbon. A candle consists mainly of compounds of carbon and hydrogen. When a burning candle is plunged into chlorine, the flame becomes red and smoky, for the hydrogen continues to burn, forming hydrogen chloride, but the carbon is liberated. Oil of turpentine is also a compound of carbon and hydrogen. When a piece of filter paper wet with warm oil of turpentine is dropped into chlorine, there is a red flash as the hydrogen burns to hydrogen chloride, while the formation of a dense cloud of soot shows that the carbon is set free.

The intense chemical activity of chlorine is dependent upon the presence in it of a trace of water vapor, which acts as a catalyst. Most of the chemical changes just described fail to occur if the chlorine is completely dry.

109. Action of chlorine upon water.

A long glass tube closed at one end is filled with chlorine water and inverted in a dish containing the same liquid (Fig. 69). When the tube is placed in sunlight, *oxygen* collects in the upper portion. The chlorine combines with the hydrogen of some of the water, forming hydrogen chloride, which dissolves, while oxygen is set free. Since the change occurs only in the presence of light, the experiment indicates that the chlorine water of the laboratory should be kept in a dark place.

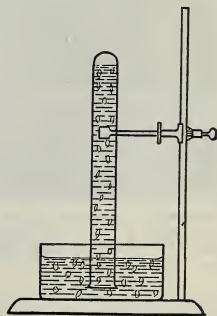
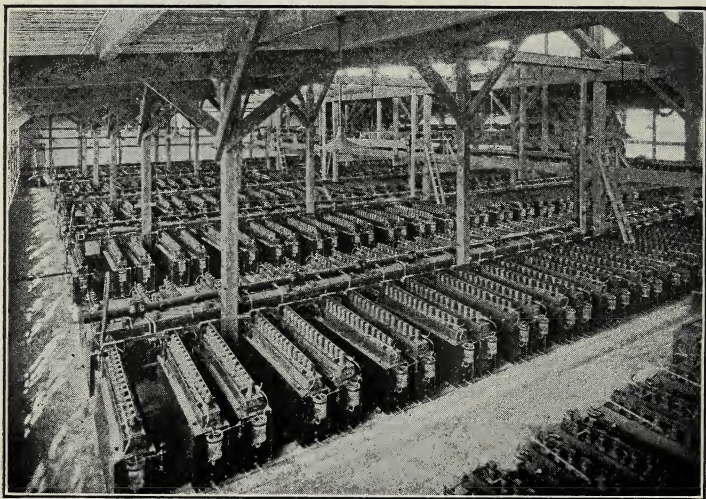


Fig. 69. Action of chlorine on water in sunlight.

110. Bleaching action. Chlorine promptly attacks and destroys most coloring matters. Flowers at once fade in it, and leaves turn to an autumnal brown and finally become colorless. Dyed cotton cloth is rapidly bleached in chlorine. A favorite experiment is to smear a page of printed matter with ordinary ink until it is illegible. Immersion in chlorine causes the printing to reappear by destroying the color of the ink



Courtesy of the Warner Chemical Co.

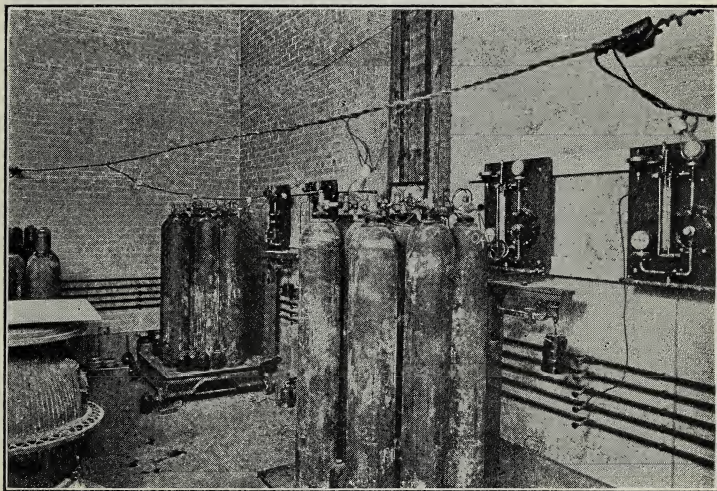
Fig. 70. Part of the plant at Edgewood Arsenal producing chlorine by the electrolysis of brine.

smeared over it. The coloring matter of printer's ink is lamp-black, a form of finely divided carbon which is not affected by chlorine.

Dried chlorine, although it often changes slightly the color of fabrics, is devoid of bleaching power. We have seen that chlorine interacts with water, liberating oxygen. This, combined with the fact that dry chlorine does not bleach, leads to the view that bleaching by chlorine may be due to *oxidation*,

the chlorine combining with the hydrogen of the water and liberating the oxygen, which attacks and burns up the coloring matter.

111. Industrial preparation. On a large scale chlorine is made by the electrolysis of salt dissolved in water. The chlorine is liberated at the positive electrode, which is made of graphite, a form of carbon. At the negative electrode, which is



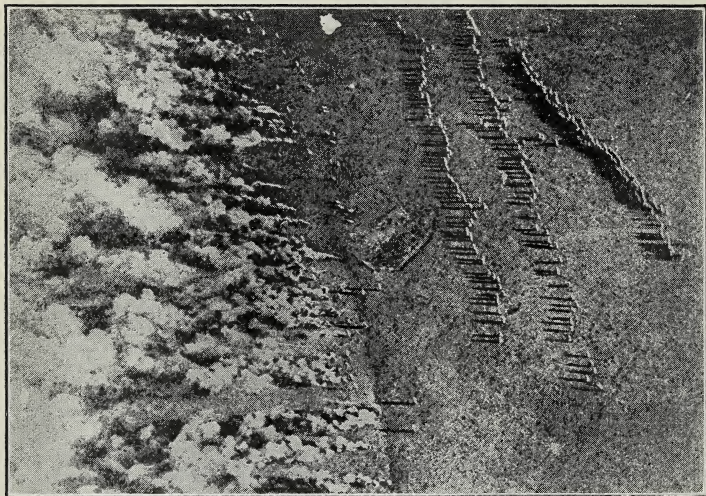
Courtesy of the Wallace & Tiernan Co.

Fig. 71. Chlorinating equipment, automatically controlled, at the Kensico Reservoir of the New York City water supply.

made of iron, *sodium hydroxide* is formed—not sodium itself, which cannot exist in the presence of water. The process will be more fully described later (§ 169).

112. Uses. The most important application of chlorine is as an agent for bleaching cotton fabrics. Linen also is bleached with it, but careful work is required to avoid injury to the fabric. Silk and wool, which would be seriously damaged by chlorine, are bleached by other means.

Because of the poisonous action of chlorine it is difficult to use the gas itself for bleaching. It is, therefore, first converted into "*bleaching powder*," or "*chloride of lime*," a white solid which is prepared by allowing slaked lime to absorb chlorine. The chlorine is liberated in the goods by treating a solution of the bleaching powder with dilute sulphuric acid.



Photograph from International Film Service.

Fig. 72. Airplane photograph of a chlorine gas attack on the Russian front early in the World War.

Chlorine destroys the life of microorganisms, but its poisonous qualities and its destructive action on metals and colored fabrics unfit it for the disinfection of rooms or of clothing. On the other hand, it is being successfully used for sterilizing water. The use of bleaching powder for this purpose has already been mentioned. Chlorine in liquid form may be used instead of bleaching powder with similar results.

Chlorine is used in the extraction of *gold* by the "*chlorination process*" from certain ores in which the metal occurs in

finely divided condition. When the powdered ore is treated with chlorine in presence of water, the gold is converted into gold chloride, which dissolves in the water. The solution is filtered to free it from the powdered rock, and the gold is recovered from it by various methods.

Chlorine was the first substance employed in *gas warfare*, which was begun by the Germans on the Ypres salient on April 22, 1915. Cylinders of liquid chlorine were placed 3 ft. apart in the German front-line trenches and the gas was allowed to escape at a time when the wind was blowing gently toward the Allied lines. The attack was entirely unexpected, being contrary to the agreement made at the Hague Conference in 1899, and it produced a shocking effect. A huge green cloud was formed, which moved slowly toward the Allied positions. When it reached them thousands of soldiers were suffocated on the spot. For a time there was a gap of a quarter of a mile in the Allied lines, and the situation was saved only by the valor of some Canadian troops who rushed into the breach with wet handkerchiefs held over their faces. Subsequently gas masks were devised as a protection against this form of attack and made an essential part of the equipment of every soldier (§ 613).

SUMMARY

Chlorine does not occur native. **Sodium chloride** or **common salt** is its most abundant compound.

Chlorine is prepared in the laboratory by oxidizing the hydrogen of hydrochloric acid to water by means of manganese dioxide or some other substance rich in oxygen.

On a large scale chlorine is obtained by the electrolysis of a solution of salt in water.

Chlorine is quite **poisonous**; in working with it great care should be taken not to inhale it or to allow it to escape into the air of the room.

Chlorine, like oxygen, is very **active**. It differs from oxygen

in the readiness with which it enters chemical combinations at ordinary temperatures.

In the form of **bleaching powder** chlorine is largely used for bleaching cotton and linen fabrics. It is applied in the extraction of gold from its ores. Liquid chlorine and bleaching powder are both employed in the **disinfection** of public water supplies.

EXERCISES

1. Give the general principle on which the preparation of chlorine in the laboratory is based.
2. What is meant by collecting a gas by *downward displacement*?
3. How is chlorine made on a large scale? What is the other product of the same process?
4. Summarize the uses of chlorine.
5. What are the two facts that have led to the belief that bleaching is a process of oxidation?
6. Why does chlorine water lose its greenish color when exposed to light? Why should the chlorine water of the laboratory be freshly prepared?
7. Why is the presence of water necessary in bleaching by chlorine?
8. How does the chemical conduct of chlorine compare with that of oxygen?
9. How is chlorine obtained in the laboratory?
10. What properties of chlorine have caused it to be employed in gas warfare? Has its high specific gravity anything to do with its fitness for this purpose?

REVIEW QUESTION

1. What is *combustion*? Can combustion occur without oxygen?

CHAPTER XIII

HYDROGEN CHLORIDE

113. Review. Some facts bearing upon the composition of **hydrogen chloride** have already been noticed. Thus, its aqueous solution yields chlorine and water when heated with substances rich in oxygen, and interacts with zinc to form zinc chloride and hydrogen. Moreover, when *chlorine water* is exposed to sunlight, hydrogen chloride and oxygen are produced. This evidence indicates plainly that hydrogen chloride, as the name signifies, is composed of hydrogen and chlorine only, and the fact that hydrogen burns in chlorine to produce hydrogen chloride puts this conclusion beyond doubt.

114. Composition of hydrogen chloride. We must now inquire how many atoms of each element are contained in the molecule of hydrogen chloride. A strong glass tube provided with a stopcock at each end (Fig. 73) is filled in the dark with

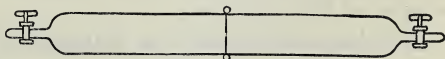
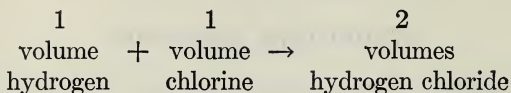


Fig. 73. Tube for the synthesis of hydrogen chloride.

mixture of equal volumes of hydrogen and chlorine. It is well to cover the tube with a wire-gauze jacket or to place a glass screen between it and the operator. When the tube is placed in sunlight, or when a piece of magnesium wire is burned near it, there is a sharp explosion, due to the formation of hydrogen chloride. After the tube has cooled, one end is placed under the surface of mercury in a dish and the stopcock at that end opened. No gas escapes and no mercury enters, showing that there has been no change in volume. But if water is employed

instead of mercury, the hydrogen chloride dissolves and the water rushes into the tube and fills it completely.

This experiment shows that the volume of the hydrogen chloride produced is equal to the sum of the volumes of the hydrogen and the chlorine:



The electrolysis of *hydrochloric acid*, which is the name given to the water solution of hydrogen chloride, supports this conclusion. The solubility of chlorine in water complicates the experiment. In the apparatus of Figure 39 some of the chlorine would dissolve in the water present, and its volume would appear to be smaller than that actually produced. Hence, special apparatus must be employed, in which the gases are measured over concentrated salt water, which dissolves very little chlorine. When the experiment is carried out in this way, the volume of the chlorine given off at the positive electrode is equal to that of the hydrogen which escapes at the negative.

Further confirmation is obtained by treating a measured volume of hydrogen chloride with sodium, which combines with the chlorine, forming *sodium chloride*. The hydrogen which remains occupies one-half the volume of the hydrogen chloride originally present. Figure 74 indicates the method of the experiment. Instead of sodium itself, a solution of sodium in mercury (*sodium amalgam*) is used. The long tube must be perfectly *dry*. It is filled over mercury with hydrogen chloride, and a little sodium amalgam is poured into it. The tube, tightly closed with a stopper, is inverted a number of times, so that the sodium amalgam repeatedly falls through the whole column of gas. When the end of the tube is immersed in water and the stopper withdrawn, the water rises half-way to the

top. That the remaining gas is hydrogen can be proved by burning it.

The composition of hydrogen chloride by weight can easily be calculated from its composition by volume. Since a liter of hydrogen weighs 0.09 gram, and a liter of chlorine 3.2 grams, chlorine is about 35.5 times as dense as hydrogen. By weight, therefore, the composition of hydrogen chloride is 1 part of hydrogen to 35.5 parts of chlorine. But the atomic weight of

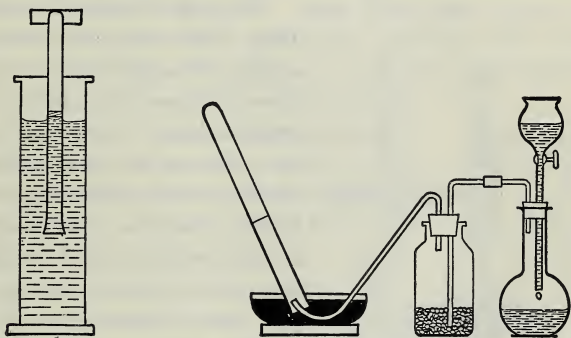
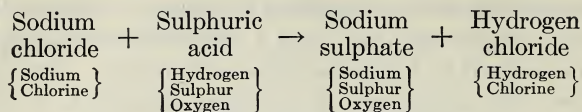


Fig. 74. Analysis of hydrogen chloride with sodium amalgam.

hydrogen is, in round numbers, 1, and that of chlorine is 35.5. Hence, the molecule of hydrogen chloride must contain 1 atom of hydrogen to 1 atom of chlorine, and its simplest formula is HCl .

115. Occurrence. Hydrogen chloride is found in the gases that issue from volcanoes. Considerable quantities exist dissolved in the waters of several South American rivers the sources of which are in volcanic districts of the Andes. The gastric juice contains 0.25 per cent of it, derived from the salt of the diet. This hydrogen chloride is indispensable in digestion; it also plays an important part as a germicide, to destroy the putrefying bacteria present in meat and prevent their development in the body.

116. Preparation. Hydrogen chloride is obtained by the action of sulphuric acid upon sodium chloride, the reaction being as follows:



Coarse rock salt is better than kitchen salt, though the latter can be used with care. The salt is placed in a flask (Fig. 75) and sulphuric acid added through the funnel tube. Since hydrogen chloride is considerably denser than air, it can be collected by downward displacement in cylinders or bottles, which must be absolutely *dry*. If hydrochloric acid is desired, the end of the exit tube is placed just above the surface of water in the cylinder; the solubility of hydrogen chloride is so great that very little of the gas will escape absorption. If the tube were allowed to dip under the surface, the water would rush back into the flask.

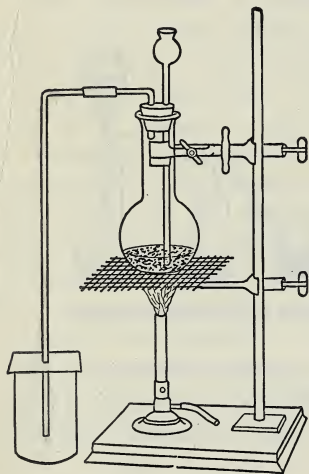


Fig. 75. Preparation of hydrogen chloride.

117. Physical properties.

Hydrogen chloride is a colorless gas with a suffocating odor. A mixture of the gas with air is irritating to the mucous membrane, but there are no serious after-effects like those which follow the inhalation of chlorine. Hydrogen chloride is $1\frac{1}{2}$ times as dense as air. Pressure or cold converts it into a liquid which boils at -83° and freezes at a still lower temperature. This liquid evolves no hydrogen

with zinc or other metals; as compared with hydrochloric acid it is an inactive substance.

The most remarkable physical property of hydrogen chloride is its extreme solubility in water. Owing to this, when the gas escapes into the air, it *fumes* or produces a fog, most noticeable in damp weather; it may also be seen when the stopper is removed from the bottle of hydrochloric acid in the laboratory. This fog is caused by the water vapor of the air, which condenses with the hydrogen chloride to form innumerable little globules of hydrochloric acid.

Water under standard conditions dissolves 500 times its volume of hydrogen chloride, and at room temperature, 450 times. This great solubility is effectively shown by the "fountain experiment" (Fig. 76). The lower vessel contains water which has been colored blue with *litmus* solution. The inverted flask is filled with hydrogen chloride. The medicine dropper contains water and serves to introduce a few drops of water into the flask and thus start the action. The hydrogen chloride at once begins to dissolve, leaving a vacuum, and the atmospheric pressure forces the water from the cylinder into the flask in a fountain. The litmus as it comes into contact with the hydrochloric acid changes from *blue* to *red*.

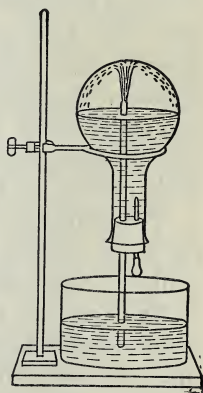


Fig. 76. Hydrogen chloride fountain.

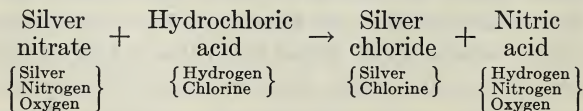
The water solution of hydrogen chloride constitutes the **hydrochloric acid** of commerce. It was formerly called "**muriatic acid**," and the old name is still occasionally used. The hydrochloric acid of the laboratory has a specific gravity of 1.2 and contains about 40 per cent of its weight of hydrogen chloride. The yellow color of many samples is due to traces of iron chloride, produced by the action of the acid upon the iron pans in which it is manufactured.

The dilute solution of hydrogen chloride has a *sour taste*. A solution which can be introduced into the mouth without danger is easily made by adding a drop or two of hydrochloric acid to a test tube full of water. It will be found that the flavor of the liquid recalls that of vinegar or lemon juice. We shall see later that the sour taste and the power of changing the color of blue litmus to red are properties possessed, not only by hydrochloric acid, but by other acids as well.

118. Chemical conduct. Dry hydrogen chloride is rather inert chemically. Hydrochloric acid, on the contrary, is a very active substance. Its interaction with *oxidizing agents*, which convert its hydrogen into water, liberating chlorine, serves as the basis of the preparation of chlorine in the laboratory. We have seen that it interacts with *zinc*, yielding zinc chloride and hydrogen. Many other familiar metals, for instance, aluminum, iron, magnesium, and tin, are converted into chlorides by hydrochloric acid, hydrogen escaping. Lead, silver, copper, and mercury are scarcely affected by it, and the noble metals, gold and platinum, do not interact with it at all.

The chlorides of the metals are chiefly solids. Most of them are freely soluble in water. *Lead chloride* is only slightly soluble. *Silver chloride* and *mercurous chloride* are insoluble.

The test for a chloride. The formation of the insoluble silver chloride serves as a *test* for hydrochloric acid or for any chloride dissolved in water. *Silver nitrate* is a white solid which is sold by the druggist under the name "lunar caustic." When nitric acid and a solution of silver nitrate are added to a liquid containing hydrochloric acid or a chloride, *silver chloride* is formed as a white, curdy solid, which darkens on exposure to light:



A solid which, like silver chloride in this experiment, appears

in a liquid as a result of a chemical change, is called a **precipitate**.

The nitric acid is added in the test described because there are many substances that, like the chlorides, give precipitates when silver nitrate is added to their solutions. No substance except hydrochloric acid or a chloride, however, will yield a precipitate when silver nitrate is added to an aqueous solution *in presence of nitric acid*.

119. Industrial preparation. On a large scale hydrochloric acid is made by the action of sulphuric acid upon sodium chloride. The salt is first placed in a round iron pan which, being at a distance from the fire, is only gently heated. About an equal weight of sulphuric acid is added. The evolution of hydrogen chloride begins at once. When the action becomes slow, the mass is raked into a hotter portion of the furnace where the remainder of the hydrogen chloride is given off. In order to dissolve the hydrogen chloride in water, the gas that escapes is led through a series of 50 or more stoneware bottles about a meter high, the gas passing from one bottle to the next through Ω -shaped tubes. A slow current of water traverses these bottles in the direction opposite to that pursued by the gas. The gas from the last bottle passes up through a tower filled with coke. Water is sprayed in at the top and trickles downward over the coke. Here the last traces of hydrogen chloride are absorbed.

120. Uses. Hydrochloric acid is employed in the manufacture of liquid glue, gelatin, glucose, and dyestuffs. It is used for cleansing the surfaces of metals before soldering. The concentrated acid is poisonous, but a dilute solution is often prescribed as a remedy for indigestion. Since this liquid acts upon the teeth, it should be taken through a glass tube to prevent contact with them. Hydrochloric acid was formerly used in large quantities for the production of chlorine, which was prepared on a large scale by the interaction of hydrochloric acid and manganese dioxide. At present, however, chlorine is

manufactured chiefly by the electrolysis of sodium-chloride solution.

As compared with sulphuric acid, the industrial importance of hydrochloric acid is small. Among the reasons for this fact there are two that are of special interest at present. *Concentrated* hydrochloric acid, that is, the saturated solution of hydrogen chloride, contains nearly two-thirds of its weight of water, which adds greatly to the expense of shipping it, since freight must be paid upon the water as well as upon the acid. Sulphuric acid, on the other hand, can readily be obtained free from water. Concentrated hydrochloric acid acts rapidly upon iron and must be therefore transported in large glass bottles, called "carboys," which are protected by a wooden case. Carboys are expensive, heavy, and fragile. On the other hand, concentrated sulphuric acid does not dissolve iron and can be cheaply and conveniently shipped in cylinders and tank cars.

SUMMARY

When a mixture of 1 volume of hydrogen with 1 volume of chlorine is exposed to sunlight or to the light of burning magnesium, there is an explosion, and 2 volumes of **hydrogen chloride** are formed.

By weight hydrogen chloride contains, approximately, 1 part of hydrogen and 35.5 parts of chlorine. Since these numbers are the approximate atomic weights of hydrogen and of chlorine, the **molecule** of hydrogen chloride must contain at least one atom of each element, and its simplest formula must be HCl.

Dry hydrogen chloride is chemically **inactive**. It is very soluble in water, and the solution is the **hydrochloric acid**, or "**muriatic acid**," of commerce.

Hydrochloric acid is very **active**. Like other acids it has a sour taste, colors blue litmus red, and yields hydrogen when it acts upon metals.

Hydrochloric acid is manufactured by the action of sulphuric acid upon sodium chloride, the hydrogen chloride evolved being led through water, which dissolves it.

EXERCISES

1. Distinguish between the meanings of the terms *hydrogen chloride* and *hydrochloric acid*.
2. What is the cause of the *fuming* of hydrochloric acid?
3. Summarize the evidence for the statement that 2 volumes of hydrogen chloride contain 1 volume of hydrogen and 1 volume of chlorine.
4. Upon what facts is based the formula HCl for hydrogen chloride?
5. What is the *test* for hydrochloric acid or for a solution of a chloride? Why is it necessary to add nitric acid?
6. Which of the following is the proper method of collecting hydrogen chloride: (a) over water; (b) upward displacement; (c) downward displacement.
7. *Any* chloride gives off hydrogen chloride when heated with sulphuric acid. Why is sodium chloride chosen as the industrial raw material?
8. What three substances are formed when hydrogen chloride acts upon sodium amalgam?
9. Describe the behavior of the following metals with hydrochloric acid: (a) zinc; (b) copper; (c) magnesium; (d) aluminum; (e) platinum; (f) silver; (g) gold.
10. Mention two properties that are common to all dilute acids.
11. What is a chloride? Discuss the solubility of the chlorides.
12. Why is hydrochloric acid more useful in the laboratory and for industrial purposes than dry hydrogen chloride?
13. What use does the tinsmith make of a solution containing hydrochloric acid?
14. A good method of making chlorine is to warm a mixture of manganese dioxide and sodium chloride with sulphuric acid. Explain.

REVIEW QUESTIONS

1. Explain the meaning of the following terms: (a) *substance*; (b) *element*; (c) *compound*; (d) *mixture*.

2. In recitations students sometimes say that copper and sulphur *mix* to form copper sulphide. Is this correct?

3. Explain with the utmost care the exact meaning of the two following statements: (a) the *specific gravity* of sulphur is 2; (b) the *atomic weight* of sulphur is 32.

4. State the following laws: (a) conservation of matter; (b) definite proportions; (c) multiple proportions.

5. Define: (a) *atom*; (b) *molecule*. Use these two ideas to explain the laws stated in Question 4.

6. What is the precise meaning of the *symbols* H and O, and of the formula H_2O ?

7. Are the atoms of all of the elements absolutely permanent?

8. State the laws of Boyle and of Charles.

9. What are the approximate percentages of nitrogen and oxygen in air by volume?

10. A student, being asked for the meaning of the formula HgO , replied that it signified 1 part of mercury and 1 part of oxygen. Criticize the answer.

CHAPTER XIV

THE MOLECULES OF THE ELEMENTS

121. Avogadro's Hypothesis. The laws of Boyle and of Charles apply to all gases alike. Whatever the chemical nature of the gas, its behavior when heated or compressed is *the same*. This significant fact distinguishes the gases sharply from the solids and the liquids, each of which conducts itself *in its own way* when heated or compressed, and for which no general laws can be framed.

The only reasonable conclusion from this is that in some respect *the structure of all gases must be alike*. This similarity cannot be in the molecules themselves, for in different gases they are composed of different materials and have different weights. The similarity, then, must be in the closeness of the packing—in the spacing of the molecules. The average distances between the molecules in hydrogen and in chlorine, for example, must be the same when the two gases are

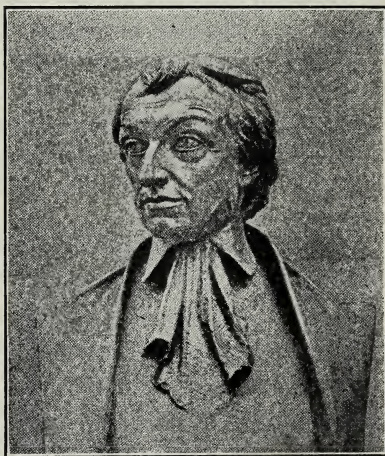


FIG. 77. AMADEO AVOGADRO (1776–1856).

Italian physicist, professor of mathematical physics in the University of Turin; advanced the hypothesis which laid the foundation for determining the number of atoms in the molecules of elementary gases.

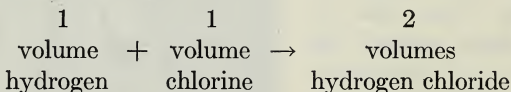
at the same temperature and pressure, and the molecules in both must approach each other to the same extent for an equal increase of pressure, and must separate to the same extent for an equal increase in temperature, so that the spacing remains the same in both so long as the two gases are at the same temperature and pressure. The same reasoning applies to all other gases.

Now, if the spacing, or closeness of packing, of the molecules is the same in all gases under the same conditions, then at equal temperature and pressure a liter of all gases must contain the same number of molecules. This statement is called **Avogadro's Hypothesis**, after the Italian *Amadeo Avogadro*, who proposed it in 1811. We may formulate it thus:

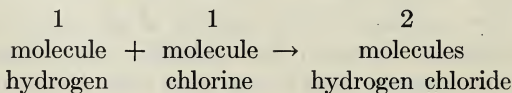
Equal volumes of all gases and vapors, measured at the same temperature and pressure, contain equal numbers of molecules.

This statement stands in such complete harmony with all that is known of the behavior of gases, vapors, and solutions that it is regarded at present, not as a mere supposition, but as a well established fact.

122. The molecule of hydrogen. Let us recall the combination of hydrogen and chlorine by volume:



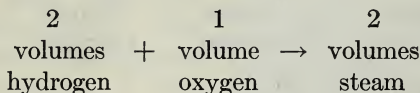
Since equal volumes of gases contain the same number of molecules, the number of molecules of chlorine must be *equal* to the number of molecules of hydrogen. For the same reason, the number of molecules of hydrogen chloride formed must be *twice* the number of molecules of hydrogen. Hence, 1 molecule of hydrogen must interact with 1 molecule of chlorine and give 2 molecules of hydrogen chloride:



Now 1 molecule of hydrogen chloride contains 1 atom of hydrogen. Since 2 molecules of hydrogen chloride have been formed from each molecule of hydrogen, *the hydrogen molecule must contain 2 atoms*. Hence, the *symbol* of hydrogen, which means *an atom of the element*, is **H**, but the *formula* is **H₂**, which denotes a *molecule composed of 2 atoms*.

123. The molecule of chlorine. The same argument applies to the chlorine. One volume of chlorine produces 2 volumes of hydrogen chloride. Since equal volumes of gases contain equal numbers of molecules, this means that 1 molecule of chlorine yields 2 molecules of hydrogen chloride. Since each molecule of hydrogen chloride contains 1 chlorine atom, *the chlorine molecule must contain 2 atoms*. Hence, the *symbol* of chlorine is **Cl**, but the *formula* is **Cl₂**, which indicates a molecule composed of 2 atoms.

124. The molecule of oxygen. The combination by volume of hydrogen and oxygen is as follows:



According to Avogadro's Hypothesis, 2 molecules of hydrogen must interact with 1 molecule of oxygen and produce 2 molecules of steam. Since the formula of steam is **H₂O**, 2 molecules of steam must contain 4 atoms of hydrogen. Thus the conclusion that the hydrogen molecule contains 2 atoms is confirmed.

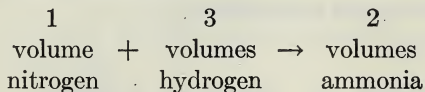
The 1 molecule of oxygen has produced 2 molecules of steam, each of which contains 1 atom of oxygen. Hence, the oxygen molecule also contains 2 atoms. The *symbol* of oxygen is **O**, but the *formula* is **O₂**.

125. The molecule of nitrogen. Ammonia water is familiar in the household. It is the aqueous solution of a gas called *ammonia*, the formula of which is **NH₃**. Under proper conditions hydrogen and nitrogen combine slowly to form ammonia.

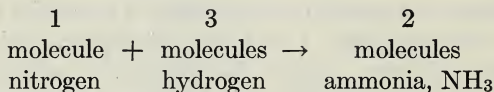
ATOMIC CONSTITUTION OF MOLECULES OF THE ELEMENTS

	Symbol (Atom)	Formula (Molecule)
Chlorine.....	Cl	Cl ₂
Hydrogen.....	H	H ₂
Nitrogen.....	N	N ₂
Oxygen.....	O	O ₂
Phosphorus.....	P	P ₄
Sulphur.....	S	S ₈
Mercury.....	Hg	Hg
Potassium.....	K	K
Sodium.....	Na	Na

The combination by volume of hydrogen and nitrogen is as follows:



Or, in molecules:



Three hydrogen molecules have yielded 6 hydrogen atoms, so that each hydrogen molecule must contain 2 atoms, the result already obtained by studying the behavior of hydrogen with chlorine and with oxygen.

One molecule of nitrogen produces 2 molecules of ammonia, each of which contains 1 atom of nitrogen. Hence the molecule of nitrogen also contains 2 atoms, and *the formula of nitrogen is N₂*. A comprehensive study of the behavior of nitrogen in its combinations with other elements confirms this conclusion.

126. Molecules of the important elements. The numbers of atoms in the molecules of some of the more important elements are indicated in the table on page 148. It will be noted that the molecules of the non-metallic elements are composed of a *group* of atoms. The molecules of the metals contain *1 atom* only.

127. Gay-Lussac's Law of Volumes. We have studied in the present chapter three instances of chemical combination between gases. We have found in each case a very simple numerical relation between the volumes of the two gases entering into combination and between the volume of each gas and that of the gaseous product. All cases of combination between gases show the same characteristic. This fact is called **Gay-Lussac's Law of Volumes**. It may be stated as follows:

When two gases combine, there is a simple relation between the volume of each entering into combination. If the product is a gas, there is a simple relation between the volume of each gas entering into combination and that of the product.

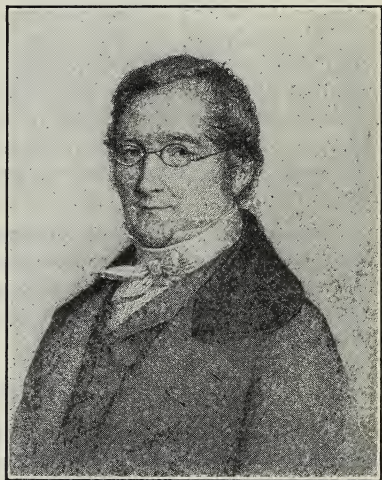


FIG. 78. JOSEPH LOUIS GAY-LUSSAC
(1778-1850).

French chemist, professor of chemistry at the Jardin des Plantes, Paris; introduced many new methods of analysis and discovered the law of the combining volumes of gases which bears his name.

This law is just what we should expect from the molecular theory. Chemical combination takes place between *molecules*, and when a gas *A* combines with a gas *B*, the number of molecules of *B* that interact with 1 molecule of *A* is always

very small. If 1 molecule of *A* unites with 1 of *B*, then 1 volume of *A* will unite with 1 volume of *B*, and so on. For all practical purposes it is as though we were able to bring a single molecule of *A* in contact with a single molecule of *B* and study the result.

SUMMARY

Equal volumes of all gases and vapors, measured at the same temperature and pressure, contain equal numbers of molecules. This is Avogadro's Hypothesis.

By studying, in the light of Avogadro's Hypothesis, the combination of gases by volume, it is possible to determine the number of atoms in the molecules of the elements that combine. It is found that in the case of the **metals** the *molecule and the atom are identical*. The molecules of the **non-metals** are, for the most part, composed of *groups of atoms*, two being the usual number.

Gay-Lussac's Law of Volumes. *Whenever two gases combine, there is a simple numerical relation between their combining volumes. If the product is also a gas, there is a simple relation between the combining volume of each gas and the volume of the product.*

EXERCISES

1. How do gases differ from solids and liquids in conduct under changes of temperature and pressure?
2. What similarity of structure in different gases is indicated by the answer to the preceding question?
3. What is Avogadro's Hypothesis?
4. Would Avogadro's Hypothesis apply to equal volumes of two gases measured under different temperatures and pressures? Explain.
5. Look up the meaning of the word *hypothesis* in a large dictionary. Chemistry and physics abound in confirmations of Avogadro's Hypothesis. Is the word "hypothesis" well chosen in the foregoing statement.
6. About how many molecules of nitrogen are there to 1 molecule of oxygen in air?

7. Explain Gay-Lussac's Law of Volumes.
8. According to Gay-Lussac's Law, what would happen if 2 volumes of hydrogen were exploded with 1 volume of chlorine?
9. Pure natural gas (*methane*) requires double its volume of oxygen to burn it completely. How many molecules of oxygen interact with 1 molecule of methane? About how many cubic feet of *air* would be needed to burn 1 cubic foot of methane?
10. Prove that the molecule of chlorine contains 2 atoms.
11. How many atoms are there in the molecule of hydrogen? Give three independent reasons for your answer.
12. If the air pressure in an automobile tire is exactly 4 atmospheres, how does the number of molecules in a cubic centimeter of the air in the tire compare with the number of molecules in a cubic centimeter of the external air?
13. Summarize briefly our knowledge of the number of atoms in the molecules of the more important elements.
14. The molecules of both elements and compounds consist of atoms. What, then, is the difference between the molecule of an element and the molecule of a compound?
15. Why is it believed that the molecule of nitrogen contains 2 atoms?

CHAPTER XV

MOLECULAR AND ATOMIC WEIGHTS

128. The weights of molecules of gases. Avogadro's Hypothesis gives us a simple means of ascertaining how much heavier the molecule of one gas is than the molecule of another. Since equal volumes of gases contain equal numbers of molecules, we have only to weigh the same volume of the two gases in turn under the same conditions of temperature and pressure. The weights will bear exactly the same relation to each other as if we had been able to weigh a single molecule of each of the two gases separately.

Sulphur dioxide is an invisible, suffocating gas which is formed when sulphur burns. It is just twice as dense as oxygen, for a liter of it weighs 2.86 grams, whereas a liter of oxygen weighs 1.43 grams. From this it follows that each sulphur-dioxide molecule must weigh just twice as much as each oxygen molecule. But the weight of the atom of oxygen is 16, and since each oxygen molecule contains 2 atoms, the weight of the molecule of oxygen must be 32. Therefore the weight of the molecule of sulphur dioxide must be 64. This is called the *molecular weight* of sulphur dioxide.

Thus, the molecular weight of sulphur dioxide can be determined by multiplying 2, which is its specific gravity referred to oxygen, by 32, which is the molecular weight of oxygen (O_2). This conclusion can be tested by adding together the weights of the atoms in the molecule of sulphur dioxide. The formula of sulphur dioxide is SO_2 ; since the atomic weight of sulphur is 32, we perceive that 64 is indeed the accepted molecular weight.

Hydrogen chloride is 1.14 times as dense as oxygen. Hence, its molecular weight must be:

$$1.14 \times 32 = 36.5$$

which corresponds to the formula HCl.

The molecular weight of a gas is equal to its specific gravity referred to oxygen multiplied by 32. We may now demonstrate this statement in general terms:

1. The specific gravity of a gas referred to oxygen is the relative weight of a liter of the gas if the weight of a liter of oxygen be taken as 1. A gas twice as dense as oxygen has a specific gravity of 2, and so on.

2. Since both the liters contain the same number of molecules, the specific gravity referred to oxygen is numerically the same as the relative weight of a single molecule of the gas if the weight of a molecule of oxygen be taken as 1.

3. But in calculating the molecular weight the weight of the molecule of oxygen is taken as 32, because it contains 2 atoms each of which weighs 16. Hence, the molecular weight of a gas is equal to 32 times its specific gravity referred to oxygen as unity. Abbreviating "molecular weight" to *M. W.*, and "specific gravity" to *Sp. Gr.*, we have,

$$M.W. = Sp. Gr. \text{ referred to } O_2 \times 32$$

129. Specific gravities referred to air. The specific gravities of gases given in text-books are referred, not to oxygen, but to air, as unity. Air is lighter than oxygen in the proportion of 10 to 11; hence the specific gravity referred to *oxygen* can be obtained by multiplying the specific gravity referred to *air* by $\frac{10}{11}$. If the specific gravity referred to air is given, we can multiply it by $\frac{10}{11}$ to get the specific gravity referred to oxygen and then multiply the product by 32 to get the molecular weight:

$$M.W. = Sp. Gr. \text{ referred to air} \times \frac{10}{11} \times 32$$

But $\frac{10}{11}$ of 32 is, in round numbers, 29. Hence,

$$M. W. = \text{Sp. Gr. referred to air} \times 29$$

*The molecular weight of a gas is equal to 29 times its specific gravity referred to air.*¹

Thus, hydrogen chloride is about $1\frac{1}{4}$ times as heavy as air; its specific gravity referred to air is 1.26. Hence its molecular weight is 1.26×29 , or 36.5, in agreement with the formula HCl. The specific gravity of steam referred to air at the same temperature and pressure is 0.621. Hence its molecular weight is 0.621×29 , or 18, which is in agreement with the formula H₂O. The specific gravity of chlorine referred to air is 2.45. Hence its molecular weight is 2.45×29 , or 71, which agrees with the formula Cl₂.

130. The formula of sulphur dioxide. When the molecular weight and the percentage composition of a substance are both known, it is a simple matter to calculate the formula. We have shown that the molecular weight of sulphur dioxide is 64. Its percentage composition is as follows:

Sulphur.....	50 per cent
Oxygen.....	50 per cent

Of the 64 parts by weight which make up the molecule, 50 per cent, or 32 parts, must be sulphur. Since the atomic weight of sulphur is 32, this corresponds to 1 atom of sulphur. The remaining 32 parts must be oxygen, and since the atomic weight of oxygen is 16, there must be 2 atoms of oxygen. Hence the formula of sulphur dioxide is SO₂.

131. The formula of hydrogen chloride. We have shown that the molecular weight of hydrogen chloride is 36.5. Its percentage composition is:

Hydrogen.....	2.74 per cent
Chlorine.....	97.26 per cent

¹ When great accuracy is required, the more exact multiplier 28.95 may be used. This is seldom necessary.

Of the total 36.5 parts by weight in the molecule, 2.74 per cent must be hydrogen; thus the hydrogen must constitute

$$36.5 \times 0.0274 = 1 \text{ part by weight}$$

This corresponds to 1 atom of hydrogen.

The parts by weight of chlorine in the molecule can be obtained by subtracting 1 from 36.5. Or the chlorine present must constitute

$$36.5 \times 0.9726 = 35.5 \text{ parts by weight}$$

so that there must also be 1 atom of chlorine present.

The formula, therefore, is HCl.

132. The formula of water. The molecular weight of water is 18, and its percentage composition is:

Hydrogen.....	11.2 per cent
Oxygen.....	88.8 per cent

Then the hydrogen in the molecule must weigh:

$$18 \times 0.112 = 2$$

which corresponds to 2 atoms.

For the oxygen:

$$18 - 2 = 16 \quad \text{or} \quad 18 \times 0.888 = 16$$

showing that the molecule contains 1 atom of oxygen. Hence the formula is H_2O .

133. Calculation of the specific gravity from the formula. The calculation of the molecular weight from the specific gravity referred to air can, of course, be reversed. For if the molecular weight of a gas is 29 times its specific gravity referred to air, then it is clear that the specific gravity referred to air must be $\frac{1}{29}$ of the molecular weight.

Thus the formula of carbon dioxide is CO_2 . Since the atomic weight of carbon is 12, this gives a molecular weight of $12 + 32$, or 44. Hence the specific gravity referred to air must

be $\frac{44}{29}$ or 1.52. Carbon dioxide is, therefore, $1\frac{1}{2}$ times as heavy as air, which explains its tendency to collect almost like a liquid in wells and to suffocate workmen who descend there without testing the air by lowering a burning candle.

*The specific gravity of a gas or vapor referred to air can be obtained by dividing its molecular weight by 29.*¹ Reducing this statement to a formula:

$$\text{Sp. Gr. referred to air} = M. W. \div 29$$

134. Volume of the gram-molecular weight. The molecular weight taken in grams is called the **gram-molecular weight**. *The gram-molecular weights of all gases occupy the same volume if measured at the same temperature and pressure. This volume is 22.4 liters at 0° C. and 760 mm.*

GRAM-MOLECULAR WEIGHTS OF IMPORTANT GASES

Name	Formula	Gram-Molecular Weight	Volume in Liters
Oxygen.....	O ₂	32	22.4
Nitrogen.....	N ₂	28	22.4
Chlorine.....	Cl ₂	71	22.4
Hydrogen chloride.....	HCl	36.5	22.4
Sulphur dioxide.....	SO ₂	64	22.4

An idea of the volume of 22.4 liters will be obtained from Figure 79. A cube of this volume would have an edge of 11.1 in. It would be slightly smaller, therefore, than a cubic foot.

Since the gram-molecular weight of all gases occupies a volume of 22.4 liters, the molecular weight of a gas can be found by simply calculating the weight of 22.4 liters of it:

$$M. W. = \text{Weight of 1 liter} \times 22.4$$

¹This is sufficient for all practical purposes. When great exactness is necessary, the figure 28.95 can be used.

Thus, the weight of 1 liter of oxygen is 1.429 grams; its molecular weight must be 1.429×22.4 , or 32, corresponding to the formula O_2 . The weight of 1 liter of hydrogen chloride is 1.63 grams; its molecular weight is 1.63×22.4 , or 36.5, which agrees with the formula HCl .

135. Specific gravity fixes molecular weight.

Students often inquire why it is necessary to determine the specific gravity of a gas in order to calculate the molecular weight, when the latter can be obtained by merely adding the atomic weights in the formula. The answer is that *the formula cannot be written until the molecular weight is known*.

Thus, the analysis of hydrogen chloride shows that it contains, in round numbers, 1 part of hydrogen and 35.5 parts of chlorine by weight. From this it follows that the molecule must contain 1 atom of hydrogen for each atom of chlorine, but the question of the total number of atoms in the molecule remains open. The formula might be HCl , H_2Cl_2 , H_3Cl_3 , or some higher multiple. *It is only when calculation from the specific gravity fixes the molecular weight at 36.5 that we know that the correct formula is HCl .*

136. Determination of atomic weights. Up to this point we have taken the atomic weights for granted, simply obtaining them from the table, which is the result of the researches of many chemists. The experimental determination of an atomic weight is a difficult task, but the principle that guides the investigator is quite simple.

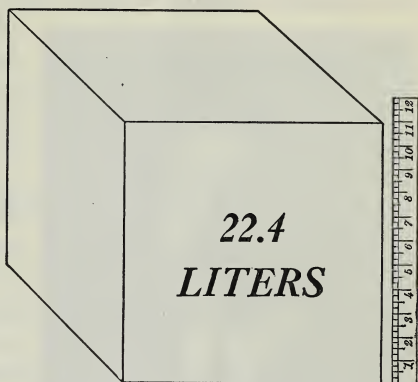


Fig. 79. Volume of the gram-molecular weight.

Let us consider, for instance, the atomic weight of copper. What is the weight of the atom of copper, if that of the atom of oxygen is taken as 16? The first step in solving this problem is to prepare a supply of pure copper, from which every trace

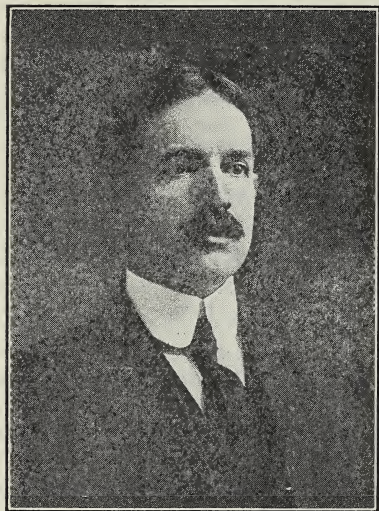


FIG. 80. THEODORE WILLIAM RICHARDS (1868-).

American chemist, professor of chemistry in Harvard University; determined the exact values of the atomic weights of more than a score of elements; awarded the Nobel prize for chemistry in 1915.

of foreign metals and other impurities has been removed. A definite quantity of this, for example, 1 gram, is weighed off with the utmost exactness. This is then converted into black copper oxide, CuO , the utmost care being taken that all of the metal is oxidized, and that not the smallest fragment of copper or copper oxide is lost. The final operation is to ascertain the increase in weight due to the addition of oxygen to the copper.

Such an experiment would show that copper combines with about one-fourth of its weight of oxygen. Let us consider an increase in weight of

0.252 gram, which is an actual result obtained with 1 gram of copper by a student in the author's laboratory. Since black copper oxide contains 1 atom of oxygen to 1 of copper, *the atomic weight of copper is that quantity which unites with 16 parts of oxygen by weight.* To calculate this we have:

Weight of oxygen : Weight of copper :: 16 : Atomic weight of copper.

0.252 : 1 :: 16 : Atomic weight of copper

The solution of this proportion gives the atomic weight of copper as 63.49. The value accepted at present is 63.57.

An atomic weight, then, is determined by carrying out a chemical change with an accurately weighed quantity of exceptionally pure material. From the change in weight the atomic weight is calculated. The conversion of an element into its oxide is a direct and favorite method of determining an atomic weight, but many other chemical changes have also been used.

SUMMARY

Let $M. W.$ = molecular weight, and $Sp. Gr.$ = specific gravity. Then:

$$M. W. = Sp. Gr. \text{ referred to air} \times 29$$

$$Sp. Gr. \text{ referred to air} = \frac{M. W.}{29}$$

$$M. W. = \text{Weight of 1 liter} \times 22.4$$

$$\text{Weight of 1 liter} = \frac{M. W.}{22.4}$$

The formula of a compound can be determined from its molecular weight and percentage composition by multiplying the molecular weight by the percentage of each element in turn.

The atomic weights of the elements are determined by carrying out chemical changes with weighed quantities of very pure substances. The changes in weight serve as a basis for the calculation of the atomic weights.

EXERCISES

1. The atomic weight of *nitrogen* is 14, and its specific gravity referred to air is 0.967. Calculate the molecular weight and formula.

2. The weight of a liter of *hydrogen* is 0.09 gram. What are its molecular weight and formula?

3. The specific gravity of *carbon dioxide* referred to air is 1.52. What is its molecular weight? If the gas contains 27.27 per cent of carbon and 72.73 per cent of oxygen what is its formula (obtain the atomic weights of carbon and of oxygen from the table)?

4. The specific gravity of *nitrous oxide* referred to air is 1.52. It contains 63.64 per cent of nitrogen and 36.36 per cent of oxygen. Calculate the molecular weight and formula.

5. The weight of 1 liter of *nitric oxide* is 1.339 grams. The gas contains by weight 46.67 per cent nitrogen and 53.33 per cent oxygen. Calculate its molecular weight and formula.

6. The specific gravity of *ammonia* referred to air is 0.586. Analysis shows that it consists of 82.35 per cent of nitrogen and 17.65 per cent of hydrogen by weight. Required, the molecular weight and formula.

7. Calculate the molecular weight and formula of *acetylene*, given that a liter of the gas weighs 1.16 grams, and it contains 92.31 per cent of carbon and 7.69 per cent of hydrogen by weight.

8. Calculate the weight of a liter of *marsh gas* from its formula CH_4 .

9. What is the weight of a liter of *carbon monoxide* gas if its formula is CO ?

10. Calculate the specific gravity referred to air of the very poisonous gas *hydrocyanic acid*, commonly called "prussic acid," which has the formula HCN .

11. The formula of the gas *phosgene* is COCl_2 . What is its specific gravity referred to air? Why was hydrocyanic acid a failure when tried in gas warfare, whereas phosgene was largely used throughout the World War?

12. One gram of pure copper when oxidized formed 1.2517 grams of copper oxide, CuO . What is the atomic weight of copper?

REVIEW QUESTIONS

1. How did Lavoisier prepare mercuric oxide?
2. How does mercuric oxide behave when heated?
3. What is the result of heating potassium chlorate? Why is

manganese dioxide added? How could you prove that the manganese dioxide was not consumed?

4. What is catalytic action? Does a substance acting catalytically appear in the chemical equation for the change?

5. According to the law of the conservation of matter, what relation must exist in a chemical equation between the sum of the weights of all the substances on the left side of the arrow and the sum of the weights of those on the right?

6. What is the relation between the total numbers of *atoms* on each side of a chemical equation? How do the numbers of atoms of *each single element* compare on the two sides?

7. Is there any general relation between the total numbers of *molecules* on the two sides of a chemical equation?

CHAPTER XVI

CHEMICAL FORMULAS AND EQUATIONS

CHEMICAL PROBLEMS

137. The formula of mercuric oxide. We have seen that Priestley, the discoverer of oxygen, prepared it by heating a brick-red powder which is now called *mercuric oxide*. The *chemical formula* is HgO .

This formula signifies a *molecule* of mercuric oxide. In any weighable quantity there are countless billions of such molecules, but all of them are exactly alike; hence the statement of the composition of a single molecule is a complete statement of the composition of the substance.

The molecule in question contains an atom of mercury, indicated by the symbol Hg, which weighs 200, and an atom of oxygen, indicated by the symbol O, which weighs 16, making 216 parts by weight in all. Hence mercuric oxide must contain $\frac{200}{216}$ of its weight of mercury and $\frac{16}{216}$ of its weight of oxygen. The percentage of mercury in mercuric oxide must be:

$$100 \times \frac{200}{216} = 92.6 \text{ per cent}$$

The percentage of oxygen is:

$$100 \times \frac{16}{216} = 7.4 \text{ per cent}$$

making a total of 100 per cent.

138. The formula of potassium chlorate. Potassium chlorate has the formula KClO_3 , which denotes a molecule contain-

ing 5 atoms—1 of potassium, 1 of chlorine, and 3 of oxygen—the weights of which are indicated below:

$$\begin{array}{rcl}
 & & K = 39 \\
 & & Cl = 35.5 \\
 & & 3 O = 48 \\
 \hline
 M. W. & = & 122.5
 \end{array}$$

For the percentages we obtain:

$$\text{Percentage of potassium} = 100 \times \frac{39}{122.5} = 31.84 \text{ per cent}$$

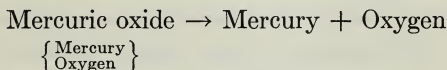
$$\text{Percentage of chlorine} = 100 \times \frac{35.5}{122.5} = 28.98 \text{ per cent}$$

$$\text{Percentage of oxygen} = 100 \times \frac{48}{122.5} = 39.18 \text{ per cent}$$

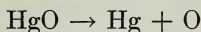
$$\text{Total} \dots\dots\dots 100.00 \text{ per cent}$$

CALCULATION OF WEIGHTS

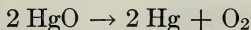
139. Chemical equations. Expressed in words, the equation for the decomposition of mercuric oxide is:



The simplest translation of this into symbols is:



But we have proved that the oxygen molecule contains 2 atoms. In order to obtain a molecule of oxygen on the right, we must take 2 molecules of mercuric oxide on the left. Thus we obtain:



This evidently means that 432 parts by weight of mercuric oxide will yield 32 parts by weight of oxygen. From these

numbers we can calculate the weight of oxygen that will be yielded by any given weight of mercuric oxide.

Consider, for instance, the following problem:

How many grams of oxygen are produced when 27 grams of mercuric oxide are heated?

The equation shows that 432 grams of mercuric oxide give 32 grams of oxygen. Hence, 1 gram of mercuric oxide must yield $\frac{32}{432}$ of a gram of oxygen, and 27 grams of mercuric oxide will yield 27 times this fraction. We have, therefore, for the solution:

$$\text{Weight of oxygen} = \frac{32}{432} \times 27 = 2 \text{ grams}$$

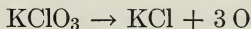
140. The decomposition of potassium chlorate. The word equation for the decomposition of potassium chlorate is:

Potassium chlorate $\rightarrow$ Potassium chloride + Oxygen

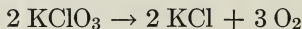
$\left\{ \begin{array}{l} \text{Potassium} \\ \text{Chlorine} \\ \text{Oxygen} \end{array} \right\}$

$\left\{ \begin{array}{l} \text{Potassium} \\ \text{Chlorine} \end{array} \right\}$

When we translate this into symbols, we obtain at first:



Here again we must remember that the oxygen is liberated in molecules which contain 2 atoms each, so that we must take 2 molecules of potassium chlorate on the left in order to obtain on the right a number of oxygen atoms that is a multiple of 2. The 6 atoms of oxygen will be grouped into 3 molecules. Thus we have:



Let us employ this equation in solving the following problem:

How many grams of oxygen are produced when 10 grams of potassium chlorate are heated?

The equation informs us that 245 grams of potassium chlorate yield 96 grams of oxygen. Hence, 1 gram of potassium chlorate will give $\frac{96}{245}$ of a gram of oxygen, and 10 grams

of potassium chlorate will yield 10 times this fraction. Thus the solution is:

$$\text{Weight of oxygen} = \frac{96}{245} \times 10 = 3.9 \text{ grams}$$

We shall now apply the equation to the solution of a problem closely related to the preceding one:

How many grams of potassium chlorate must be heated to produce 12 grams of oxygen?

Since 245 grams of potassium chlorate give 96 grams of oxygen, to yield 1 gram of oxygen $\frac{245}{96}$ grams of potassium chlorate will be needed, and to obtain 12 grams of oxygen we must take 12 times this quantity; hence we have:

$$\text{Weight of potassium chlorate} = \frac{245}{96} \times 12 = 30.6 \text{ grams}$$

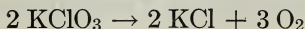
CALCULATION OF VOLUMES OF GASES

141. Oxygen from potassium chlorate. Let us now consider the weight of potassium chlorate needed to produce a required volume of oxygen, as in the following problem:

10 liters of oxygen are needed. How many grams of potassium chlorate must be heated?

We might solve this problem by first obtaining the weight of the oxygen needed. This could be done by multiplying the weight of 1 liter of oxygen by 10. The weight of potassium chlorate needed to produce this weight of oxygen could then be calculated as in the problem just discussed.

This, although sometimes useful, is a roundabout method, involving more arithmetical work than is necessary. The equation



indicates that 2 gram-molecular weights (245 grams) of potassium chlorate give 3 gram-molecular weights of oxygen. Since

a gram-molecular weight of any gas fills a volume of 22.4 liters, the total volume of the oxygen in the equation (3 O_2) is 22.4 liters $\times 3$, or 67.2 liters. But if 245 grams of potassium chlorate give 67.2 liters of oxygen, to produce 1 liter the weight of potassium chlorate needed will be $\frac{245}{67.2}$, and to obtain 10 liters of oxygen 10 times this quantity must be used. The solution, therefore, is:

$$\text{Weight of potassium chlorate} = \frac{245}{67.2} \times 10 = 36.46 \text{ grams}$$

A very similar problem is the following:

How many liters of oxygen are produced when 61.25 grams of potassium chlorate are heated?

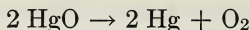
Since 245 grams of potassium chlorate produce 67.2 liters of oxygen, 1 gram will give $\frac{67.2}{245}$ of a liter, and 61.25 grams will yield 61.25 times this volume. The solution becomes:

$$\text{Volume of oxygen} = \frac{67.2}{245} \times 61.25 = 16.8 \text{ liters}$$

142. Oxygen from mercuric oxide. Let us now solve the following problem:

How many liters of oxygen can be made by heating 50 grams of mercuric oxide?

From the equation



we perceive that 432 grams of mercuric oxide yield 1 gram-molecular weight, 22.4 liters, of oxygen. Hence the solution is:

$$\text{Volume of oxygen} = \frac{22.4}{432} \times 50 = 2.59 \text{ liters}$$

CORRECTION OF VOLUME FOR TEMPERATURE AND PRESSURE

143. In all problems involving volumes the gases are supposed to be at 0° C. and 760 mm. unless the conditions under

which they are measured are stated. If the volume under some other temperature and pressure is desired, the correction is made by the methods explained in Chapter V. Take, for example, the following problem:

How many liters of oxygen at 27° C. and under a pressure of 740 mm. can be made by heating 27. grams of mercuric oxide?

For the volume of the oxygen at 0° C. and 760 mm. we have, by the method of the preceding problem:

$$\text{Volume} = \frac{22.4 \times 27}{432} \text{ liters}$$

This must now be corrected for temperature and pressure. The absolute temperature of 27° C. is 300°. Therefore, the temperature correction will be made by multiplying by $\frac{300}{273}$. The pressure correction will be $\frac{760}{740}$. For the final volume we obtain:

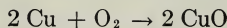
$$\text{Volume} = 22.4 \times \frac{27}{432} \times \frac{300}{273} \times \frac{760}{740} = 1.58 \text{ liters}$$

The use of four-place logarithms greatly simplifies such calculations. A table of logarithms is given in the Appendix.

EQUATIONS FOR CHEMICAL CHANGES IN PRECEDING CHAPTERS

144. The following list contains the equations for the more important chemical changes already studied. In each case reference is made to the section where the reaction in question is discussed.

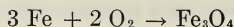
1. *Heating copper in the air (§ 5):*



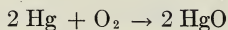
2. *Heating copper with sulphur (§ 6):*



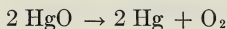
3. *Heating iron in air* (§ 11):



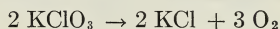
4. *Heating mercury in air* (§ 13):



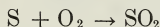
5. *Decomposition of mercuric oxide* (§ 13):



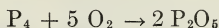
6. *Preparation of oxygen from potassium chlorate* (§ 26):



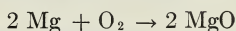
7. *Burning of sulphur in oxygen* (§ 28):



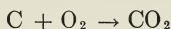
8. *Burning of phosphorus in oxygen* (§ 28):



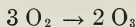
9. *Burning of magnesium in oxygen* (§ 28):



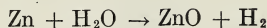
10. *Burning of charcoal in oxygen* (§ 28):



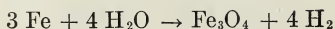
11. *Formation of ozone* (§ 39):



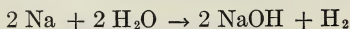
12. *Heating zinc in steam* (§ 63):



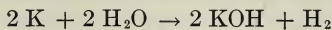
13. *Heating iron in steam* (§ 63):



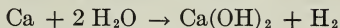
14. *Interaction of sodium and water* (§ 64):



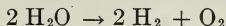
15. *Interaction of potassium and water (§ 64):*



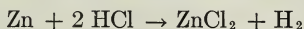
16. *Interaction of calcium and water (§ 64):*



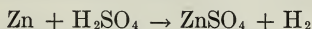
17. *Electrolysis of water (§ 65):*



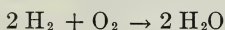
18. *Preparation of hydrogen from zinc and hydrochloric acid (§ 66):*



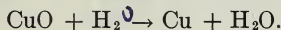
19. *Preparation of hydrogen from zinc and sulphuric acid (§ 66):*



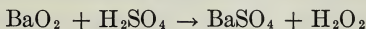
20. *Explosion of a mixture of hydrogen and oxygen (§ 69):*



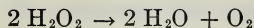
21. *Reduction of copper oxide by hydrogen (§ 69):*



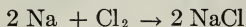
22. *Preparation of hydrogen peroxide from barium peroxide and sulphuric acid (§ 94):*



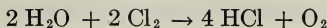
23. *Decomposition of hydrogen peroxide into water and oxygen (§ 64):*



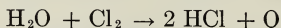
24. *Burning of sodium in chlorine (§ 108):*



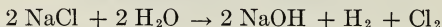
25. *Action of chlorine upon water (§ 109):*



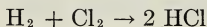
26. *Bleaching by chlorine* (§ 110) (in bleaching the free atoms of oxygen oxidize the coloring matter, instead of being liberated as molecules of O_2):



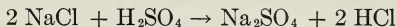
27. *Electrolysis of sodium chloride dissolved in water* (§ 111):



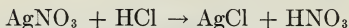
28. *Combination of hydrogen and chlorine* (§ 114):



29. *Production of hydrogen chloride from sodium chloride and sulphuric acid* (§ 116):

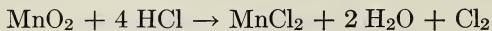


30. *Test for hydrochloric acid, or for any soluble chloride, with silver nitrate* (§ 118):



145. The balancing of equations. The writing of equations like those just given is not a matter of memory. First of all, of course, the formulas of the substances that enter into the change and of those that are produced must be known. If this information is at hand, the working out of the equation is an easy task, requiring only the simplest arithmetic.

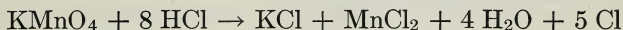
Let us take as an example the preparation of chlorine by oxidizing the hydrogen of hydrogen chloride to water by means of manganese dioxide, MnO_2 . To form water with the 2 oxygen atoms of the manganese dioxide, 4 atoms of hydrogen will be required. This makes it necessary to introduce 4 HCl on the left-hand side of the equation. It follows that 2 H_2O will appear among the products. Moreover, we know that the chlorine must be given off in molecules, each of which contains 2 atoms, and that half of the total chlorine remains, combined with the Mn as manganese chloride, $MnCl_2$. The only equation that satisfies these requirements is:



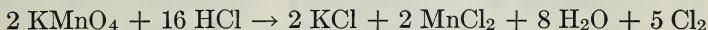
The same kind of reasoning applies to more complex cases. Potassium permanganate, KMnO_4 , though more expensive than manganese dioxide, is much more convenient for generating small quantities of chlorine and is often used for the purpose. From the presence of 4 oxygen atoms it is plain that the potassium permanganate and the hydrochloric acid must enter the change in the proportion:



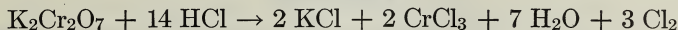
The formation of 4 H_2O is obvious. Also we know that potassium chloride is KCl , that manganese chloride is MnCl_2 , and that both of these will be formed by the union of the chlorine with the atoms of potassium and manganese. This leaves 5 atoms of chlorine to be set free:



But the chlorine is not liberated in atoms, but in molecules, Cl_2 . To take this into account we must double the entire expression. Thus we get the final correct equation:



146. *Potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, is another cheap oxidizing agent which is used in the preparation of chlorine. Since the formation of water with 7 atoms of oxygen will require 14 atoms of hydrogen, we perceive at once that 14 HCl must interact with 1 $\text{K}_2\text{Cr}_2\text{O}_7$, and that 7 H_2O and 2 KCl will result. The formula of chromium chloride is CrCl_3 , and 2 molecules of it will be obtained. This leaves 6 Cl , which will be liberated as 3 Cl_2 . Thus the equation is:



After an equation is written, it should be inspected to make sure that it is free from mistakes. The most common errors can be detected by remembering (1) that *matter is indestructible*

and (2) that *the elements cannot be transformed into each other in ordinary chemical changes*. Therefore:

The number of atoms of each element must be the same on the right side of the equation as on the left.

Applying this rule to the equation above, we find on each side 2 K, 2 Cr, 7 O, 14 H, and 14 Cl. Hence the equation is correctly *balanced*.

Finally, a chemical equation must apply to a *real chemical change*. This distinction between chemical and algebraic equations is important. For example, an equation might be written in which gold was represented as dissolving in hydrochloric acid, with escape of hydrogen. The equation might balance perfectly, and yet to the chemist it would be absurd, since, as a matter of fact, hydrochloric acid has no action whatever upon gold.

SUMMARY

To calculate the percentage composition from the formula of a substance, multiply the weight of each element in the molecule by 100 and divide by the molecular weight. It is usual to carry out the calculation to two decimal places. The results for all the constituents should add to 100.

In constructing a chemical equation:

1. Every formula used should be that of a real substance which has been proved by experiment either to enter the change or to be produced by it.
2. The number of atoms of each element must be the same on the right side of the equation as on the left.

EXERCISES

1. Calculate the percentage composition of *silver acetate*, $\text{AgC}_2\text{H}_3\text{O}_2$.
2. What is the percentage composition (a) of *silver chloride*, AgCl ; (b) of *silver sulphide*, Ag_2S ?

3. How many grams of *zinc oxide*, ZnO , are produced by burning 5 grams of zinc?
4. How many grams of *magnesium oxide*, MgO , are formed when 12 grams of magnesium ribbon are burned?
5. What would be the increase in weight of 30 grams of iron if converted (a) into *ferrous oxide*, FeO ; (b) into *ferric oxide*, Fe_2O_3 ?
6. How many grams of chlorine can be obtained by the electrolysis of a solution containing 100 grams of sodium chloride?
7. What is the cost of preparing a kilogram of hydrogen from zinc and sulphuric acid? Assume that the price of zinc is 44 cents per kilogram, and that of sulphuric acid 6 cents per kilogram.
8. What is the weight of the hydrogen which escapes when 0.5 gram of sodium acts upon water?
9. How many grams of oxygen can be obtained by the catalytic action of manganese dioxide upon 100 grams of a 5 per cent solution of hydrogen peroxide?
10. How many liters of gaseous hydrogen chloride can be obtained by the action of sulphuric acid upon 25 grams of sodium chloride?
11. A solution of hydrochloric acid was made by dissolving 450 liters of hydrogen chloride in 1 liter of water. What was the percentage of hydrogen chloride by weight in the liquid?
12. How many cubic centimeters of oxygen are obtained when 1 gram of potassium chlorate is heated with manganese dioxide?
13. How many grams of water are formed by the burning of 5 liters of hydrogen?
14. How many liters of hydrogen must be burned to yield 5 grams of water?
15. How many grams of sodium chloride must be dissolved in water and electrolyzed to produce 10 liters of chlorine?
16. 16 c.c. of hydrogen were mixed with 20 c.c. of chlorine and the mixture caused to explode. What volumes of what gases remained in the vessel?
17. Hydrogen was burned in chlorine and the hydrogen chloride produced was collected. It weighed 146 grams. How many grams of each gas had been consumed?

18. 32.75 grams of zinc are dissolved in hydrochloric acid. How many grams of zinc chloride and how many of hydrogen are produced?

19. 500 c.c. of hydrogen escaped when a piece of sodium was placed in water. What was the weight of the sodium?

20. How many grams of hydrochloric acid containing 20 per cent of hydrogen chloride are needed to liberate 100 grams of chlorine with manganese dioxide?

CHAPTER XVII

SODIUM (Na = 23); METALS AND NON-METALS

SODIUM

147. Occurrence. Sodium is a very active metal and, therefore, does not occur native. Its compounds, however, are widely distributed, so that it is placed eighth among the elements in order of abundance and makes up 2.43 per cent of the crust of the earth. It is contained in many common rocks, especially in those of igneous origin. The most abundant compound is *sodium chloride* (common salt).

148. Preparation. When the electric current is passed through melted *sodium hydroxide* ("caustic soda"), oxygen is liberated at the positive electrode and hydrogen and sodium at the negative electrode:



The positive electrode is the place where the current *enters* the liquid. It is also called the **anode**. The negative electrode,

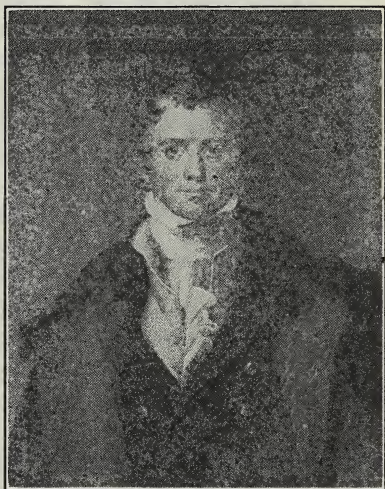


FIG. 81. SIR HUMPHRY DAVY
(1778-1829).

English chemist, professor of chemistry in the Royal Institution; discovered sodium, potassium, and other elements, explained the chemical nature of acids, and invented the miner's safety lamp.

also termed the **cathode**, is the place where the current *leaves* the liquid. It was by this method that Sir Humphry Davy in 1807 discovered sodium.

Figure 82 is a diagram of the apparatus used in making sodium on a large scale. The melted sodium hydroxide is contained in an iron cylinder, through the bottom of which the cathode *c* projects. Several anodes *aa* surround the cathode. The sodium, being lighter than the molten hydroxide, collects in a cylindrical vessel *v*, which is placed over the cathode. This serves to protect the sodium from the oxygen that is formed at the anode. The heat produced by the passage of the current keeps the sodium melted, though gas burners are provided in case additional heat is needed.

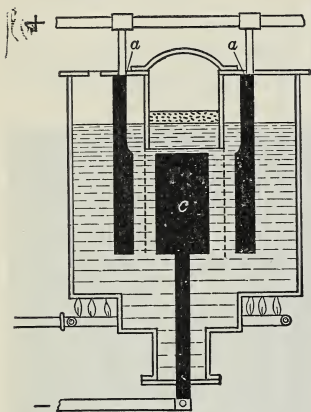


Fig. 82. Apparatus for the preparation of sodium.

149. Physical properties. Sodium is a white, waxy metal, soft enough to be cut with a knife. It has a brilliant lustre when

freshly cut, which fades at once because of the action of the water vapor of the air on the metal. When sodium is sealed up in a glass tube from which the air has been displaced by a current of dry hydrogen, the lustre is permanent. Sodium is slightly less dense than water, the specific gravity being 0.98. It is an excellent conductor of electricity and of heat.

Heated in the absence of air, sodium melts a little below the boiling point of water to a liquid which looks like mercury. This liquid boils at a red heat, passing into a blue vapor, the specific gravity of which shows that the sodium molecule contains but 1 atom. The symbol of sodium is Na, and hence the formula is Na also.

150. Chemical conduct. Sodium is far more active than the ordinary metals. When exposed to air, it becomes moist and is converted, first into sodium hydroxide, and then into a white mass of sodium carbonate. For this reason it is preserved under kerosene or benzine.

Heated in air, it burns rapidly to a grayish-white powder of *sodium oxide*, Na_2O . By the slow combustion of gently heated sodium *sodium peroxide*, Na_2O_2 , is formed. The interaction of sodium with water and its brilliant combustion in chlorine have already been described.

151. Test for sodium. Sodium and all of its compounds color the flame of the Bunsen burner a brilliant yellow. The sodium compound does not *burn*. It merely vaporizes in the flame of the burning gas and colors it. This behavior is useful as a *test* for sodium, but the student should remember that sodium is widely distributed and that the delicacy of the test is extreme. Almost any chemical in the laboratory contains enough sodium to color the flame for a few moments. Notable quantities of sodium color the flame bright yellow for a long time.

152. Uses. The unfitness of sodium for the structural purposes which we associate with the common metals is plain. All its uses are *chemical*. It is employed in the manufacture of dyestuffs and other complex carbon compounds. Large quantities are consumed in the manufacture of sodium peroxide and of *sodium cyanide*, NaCN , both of which are important commercial products.

METALS AND NON-METALS

153. Distinctive properties of metals and non-metals. The elements can be classified into *metals* and *non-metals*. Sodium, iron, and copper are typical metals. Fresh or polished surfaces of the metals have a peculiar lustre called the *metallic lustre*. This is due to the fact that, as they are much more opaque than

other substances, fresh or polished surfaces reflect regularly most of the light that falls upon them. The metals are more or less *ductile*—that is, they can be drawn into wire, and they are more or less *malleable*, which means that they can be beaten out under the hammer. When a compound of a metal is dissolved in water and electrolyzed, the metal deposits at the *cathode*. Sixty or more of the elements are metals. All of the metals are solids except mercury, which is a liquid.

Oxygen, chlorine, and sulphur are excellent examples of true *non-metals*, of which there are 20 among the elements. Of these, 11 are gases and 9 are solids, only one, *bromine*, being a liquid. The non-metals are far more transparent than the metals, and hence they do not possess the true metallic lustre. They are inferior to the metals in ability to conduct electricity and heat. The solid non-metals are brittle and exhibit no trace of malleability or ductility. During electrolysis the non-metals are liberated at the *anode*.

154. Light and heavy metals. During the Middle Ages the metals were divided into the "*base metals*," like copper and lead, which lost their lustre and were converted into oxides when heated in the air, and the "*noble metals*," which were not changed into oxides when heated and were said to stand the "fire test." Silver and gold were the typical noble metals. It is clear that the difference is merely that they are less active than the base metals.

A more modern classification of the metals is into "light" and "heavy" metals. The *light metals* are those of which the specific gravity is less than 5. Sodium (specific gravity, 0.98) and potassium (specific gravity, 0.86) are perfect examples. The light metals are greatly inferior to the heavy metals in ductility, malleability, and tenacity (toughness). They are intensely active. They burn energetically when heated in the air, and most of them are rapidly converted by water into their hydroxides, hydrogen escaping. Their physical and chemical properties unfit them for structural uses.

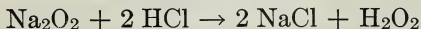
The *heavy metals* are those of which the specific gravity is greater than 5. This class includes almost all the familiar important metals, such as iron (specific gravity, 7.8), copper (specific gravity, 8.9), lead (specific gravity, 11.4), and gold (specific gravity, 19.3). They are greatly superior to the light metals in tenacity, malleability, and ductility, and they are much less active, so that air and water act slowly upon them, if at all. Some of them are structural materials of enormous importance.

Aluminum occupies an exceptional position. Its low specific gravity (2.64) places it with the light metals; yet air and water have little effect upon it, and it is successfully employed for a great variety of purposes. The cause of these peculiar properties will be explained later (§ 428).

COMPOUNDS OF SODIUM

155. Sodium peroxide, Na_2O_2 . When sodium, cut into slices, is heated in a current of air to 300° , *sodium peroxide*, Na_2O_2 , is formed. This is a light-yellow powder, which is a violent oxidizing agent. Care in handling and storing it is required, to avoid danger of fire.

When sodium peroxide is dissolved in water or treated carefully with acids, hydrogen peroxide is formed:

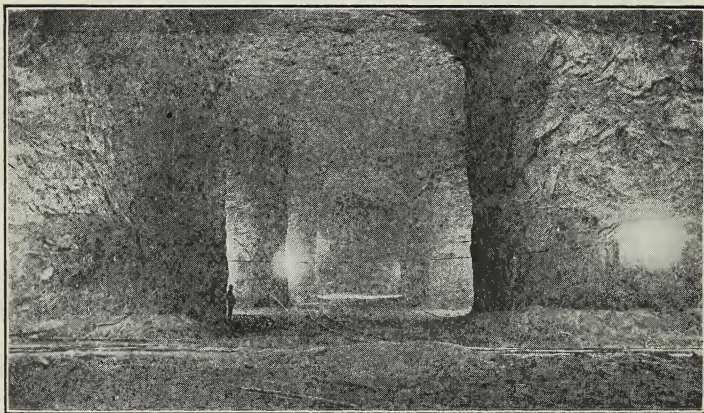


For this reason sodium peroxide is produced commercially on a large scale and is used in bleaching wool and silk.

156. Sodium chloride, NaCl : Occurrence. Sodium chloride, *common salt*, is by far the most abundant compound of sodium. Great beds of rock salt are found in New York, West Virginia, Louisiana, Michigan, Kansas, Utah, Nevada, and California. Michigan is the largest producer, but the New York salt is purer and commands a higher price. In Colorado salt is found as a crust over a lake of brine. This salt is cut

like ice, washed in the water of the lake, and crushed for market. Extensive deposits of rock salt exist in many European countries.

Much of the salt produced in the United States is obtained by the evaporation of the water of *salt springs*, which are numerous in the middle and western states. The water of the Great Salt Lake, in Utah, which has an area of 2,000 sq. miles, contains 20 per cent of salt. The water of the ocean carries 2.5 per cent of salt, and the salt in the earth's sea water, if



Photograph from Ewing Galloway.

Fig. 83. Interior of a Kansas salt mine; the huge pillars of solid rock salt are left to support the roof.

extracted, would have a total volume of 5 million cubic miles. Thus there is enough salt in the ocean to cover the United States to the depth of over a mile and a half, or the whole world to the depth of 112 ft.

157. Production of salt. Pure rock salt is a colorless, transparent solid, which is easily distinguished from other minerals by its cubical crystallization, by the fact that it breaks along the faces of a cube when struck, by its solubility in water, and by its taste. Such salt requires only to be crushed to fit it for use. Usually, however, rock salt is colored reddish by

iron compounds and contains gypsum, clay, and other insoluble substances. The purification of rock salt is carried out by treating the crushed mineral with water. The insoluble impurities are allowed to settle, and the clear salt solution is drawn off and evaporated, in shallow, steam-heated iron pans 40 to 100 ft. long and 10 to 25 ft. wide, to obtain the solid salt. Similar pans are also employed to evaporate the waters of the salt springs from which the greater part of the salt of the United States is produced. In some works the evaporation is carried out in vacuum pans similar to those used in sugar refining (§ 585).



Courtesy of the U. S. Geological Survey.

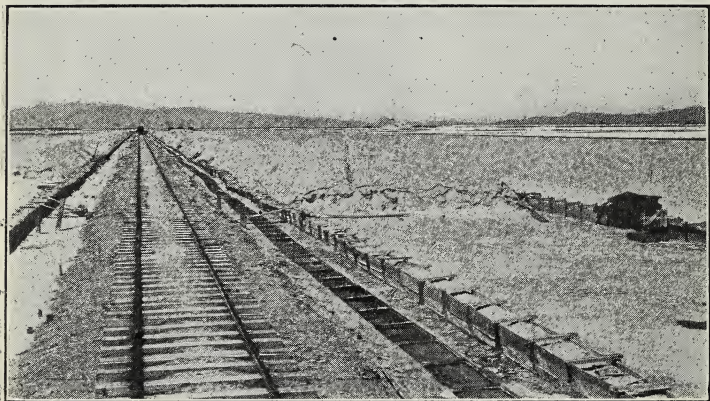
Fig. 84. Evaporating brine from salt springs in northern New York.

158. Salt from sea water. Sea water cannot be profitably evaporated for salt by artificial heat, because it does not contain enough salt to repay the expenditure for fuel. Hence the heat of the sun must be utilized. The climate of California and of the countries bordering upon the Mediterranean is especially suited to the process. Large shallow basins dug near the strand are lined with hard clay or cement. Sea water is admitted in the spring and is allowed to evaporate until saturated with salt. Meanwhile clay and gypsum separate from it. The liquid is then run into another basin, where the evaporation is continued until most of the salt is deposited. The crusts of salt are raked out and piled in heaps to drain and dry. This salt averages 95 per cent pure. When the deposited salt begins to be quite impure by reason of the deposition with it of other dissolved substances, the liquid is run into a third

basin in which a lower grade of salt is obtained. Salt is produced by this method at San Francisco and Los Angeles and at Saltair, Utah, on the Great Salt Lake.

The United States produces more salt than any other nation, the annual output being over 30 million barrels, valued at upwards of \$2,500,000.

159. Properties of sodium chloride. Sodium chloride is a white granular substance consisting of cubical crystals. It



Photograph from Ewing Galloway.

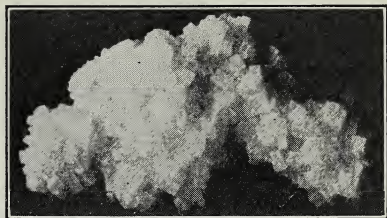
Fig. 85. Solar evaporation of salt from the water of the Great Salt Lake at Saltair, Utah.

melts at a red heat and vaporizes rapidly at a somewhat higher temperature, as can be seen by sprinkling some salt on a hot fire. The solubility of sodium chloride in water can best be obtained from the "curve" in Figure 87. The solubility curve for "nitre," which is *potassium nitrate*, KNO_3 , is given also for comparison. It will be noted that water dissolves about one-third of its weight of salt, and that the quantity is almost the same at all temperatures, which is most unusual. On the other hand, the solubility of nitre is seen to increase rapidly with rising temperature, which is the ordinary behavior

of solids. The ice that forms on the surface of salt water is *free from salt*. The same thing is true of dilute solutions generally. *The ice that separates when a dilute solution begins to freeze contains none of the solute.*

160. Uses of sodium chloride.

Salt is a necessity in the diet. In its absence the hydrochloric acid disappears from the gastric juice, and the work of the stomach is deranged. However, the quantities of salt that are usually employed for flavoring food are far



Courtesy of the U. S. Geological Survey.

Fig. 86. Crystals of sodium chloride.

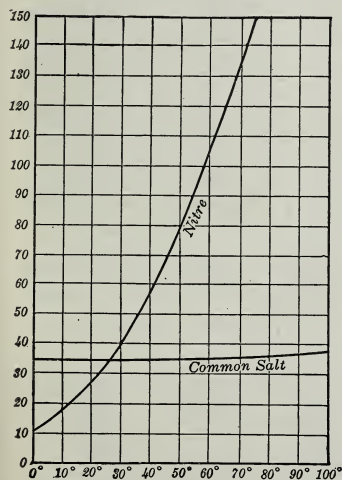


Fig. 87. Solubility curves of salt and nitre.

greater than can be utilized in the body. Kitchen salt contains about 97.5 per cent of sodium chloride, the balance being chiefly *calcium sulphate*, CaSO_4 , and water. A trace of *magnesium chloride*, MgCl_2 , is present, and this increases the tendency of the salt to deliquesce in damp weather; but even pure sodium chloride (or any other soluble solid) will become moist if the humidity approaches 100 per cent. The "free-running" salt contains 1 per cent of *magnesium carbonate*, a fine, loose, white powder, which coats the salt crystals

and makes them slide easily upon each other. An impure, "coarse" grade of salt is used as an addition to the food of cattle and is mixed with ice to form a freez-

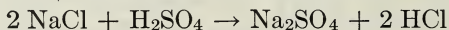
ing mixture in the production of ice cream and similar materials.

The largest market for salt is in the chemical industries. As the cheapest compound of *chlorine*, it serves as the basis of the preparation of chlorine, as well as of hydrochloric acid, bleaching powder, and many other chlorine compounds. As the cheapest compound of *sodium*, it forms the raw material for the great industries based upon sodium compounds, such as the production of *sodium carbonate*, *sodium hydroxide*, *sodium sulphate*, and *borax*. Salt is employed in glazing the cheaper grades of pottery, and it forms indirectly the foundation of the soap industry and of the glass industry, for the sodium compounds which are consumed in enormous quantities in the manufacture of these products are prepared from salt.

A fraudulent use of salt is in the so-called "fuel-saving compounds," which are sold, under various attractive names, in the form of white powders to be dissolved in water and sprinkled on coal before burning it. They consist mainly of salt, which colors the flame of the burning coal bright yellow and gives the illusion of a more energetic combustion. Combustion is really somewhat hindered by the use of these substances.

Sodium bromide, NaBr, is a white powder resembling sodium chloride in appearance and taste. It is freely soluble in water. It is much employed in medicine, especially in diseases of the nervous system.

161. Sodium sulphate, Na₂SO₄. Sodium sulphate is made by the action of sulphuric acid on sodium chloride:

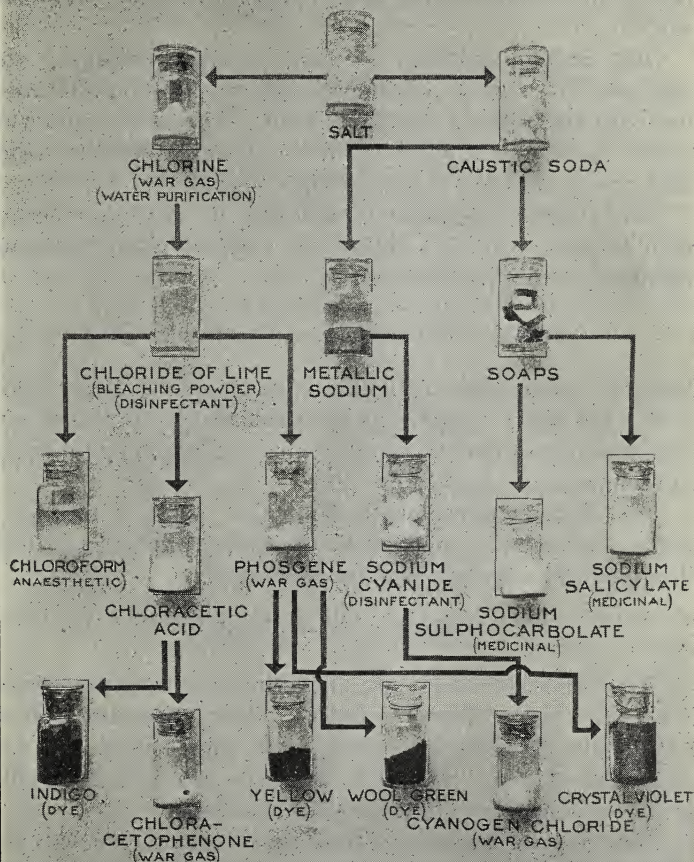


It is a white solid which is used in the manufacture of other sodium compounds, especially of *sodium carbonate*, Na₂CO₃. The chief market for sodium sulphate is in the glass industry.

Sodium sulphate is freely soluble in water and has a remarkable tendency to form a supersaturated solution. When the

SALT PRODUCTS

IN WAR AND PEACE TIME INDUSTRIES



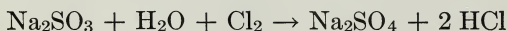
Courtesy of the National Research Council.

Fig. 88. Typical products based upon salt as raw material.

solution crystallizes, the solid that separates is found to contain 10 molecules of water of crystallization and to possess the formula $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. These crystals have long been employed in medicine under the druggist's name of "**Glauber's salt.**"

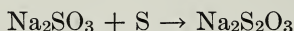
162. Sodium sulphite, Na_2SO_3 . Sodium sulphite, when deposited from water solution, forms colorless crystals which have the composition $\text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O}$. *Anhydrous* sodium sulphite, Na_2SO_3 , is a white powder. Both are used in photography as an addition to the *developer* (§ 362).

When sodium sulphite is dissolved in water and treated with chlorine, oxidation to *sodium sulphate* takes place, with formation of hydrochloric acid:



For this reason sodium sulphite is employed in paper making and in the textile industry as an "**antichlor.**" It is used after the bleaching to remove traces of chlorine, which might remain in the goods and weaken the fibre.

163. Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. When a solution of sodium sulphite is boiled with powdered sulphur, the latter dissolves and *sodium thiosulphate* is formed:



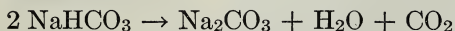
The crystals that are deposited have the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$. These colorless, glassy crystals are the **hypo** of the photographer, which is the chief constituent of the *fixing bath* (§ 363). Sodium thiosulphate, like sodium sulphite, is largely used as an antichlor after bleaching.

164. Sodium carbonate, Na_2CO_3 . Sodium carbonate is a white powder which has a bitter, nauseous taste and is poisonous. It melts without decomposition at a red heat. Sodium carbonate is known in trade as "**soda ash**" or simply as "**soda.**" It is a commercial product of the first importance, being used

in enormous quantities in the glass industry, in making sodium hydroxide and other sodium compounds, in softening "hard" waters, in laundry work, in photography, and for countless other purposes. The total production of sodium carbonate averages 3 pounds annually per person for the entire population of the earth.

Sodium carbonate is freely soluble in water. When a warm solution is cooled, glassy crystals separate, the composition of which is expressed by the formula $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. This is the **washing soda** of the household. When kept for a time exposed to the air, the crystals effloresce, losing their water of crystallization and falling to a white powder. Since crystallized sodium carbonate contains nearly two-thirds of its weight of water, it is more profitable to prepare the crystals in the locality where they are to be consumed than to ship them for long distances.

165. Sodium hydrogen carbonate, NaHCO_3 . Sodium hydrogen carbonate is the **baking soda**, "**saleratus**," or **sodium bicarbonate** of the household. It is a white powder, resembling sodium carbonate in appearance, but not at all in other properties. It has a pleasant saline taste. It is not poisonous, being used in the preparation of pastry and as a remedy for some forms of indigestion. It is far less soluble in water than is sodium carbonate, and, unlike the latter, it is decomposed by a gentle heat, yielding sodium carbonate, water, and carbon dioxide, the carbon dioxide escaping as a gas:



The ease with which carbon dioxide escapes from baking soda explains the use of the latter in the kitchen. The carbon dioxide, subdivided into innumerable bubbles during the kneading, is caught and held by the tenacious dough. Each bubble expands in the oven, and thus the finished cake is made porous and "light."

166. The chemical fire extinguisher. A given weight of sodium hydrogen carbonate yields twice as much carbon dioxide when treated with an acid as it does when merely heated; with sulphuric acid, for example:



The chemical fire extinguisher (Fig. 89) contains a bottle of sulphuric acid and a solution of sodium hydrogen carbonate so arranged that the two are mixed when the apparatus, at the time of use, is inverted. The pressure of the carbon dioxide propels the stream, and the gas also plays a part in excluding oxygen from the combustion. Moreover, a solution of sodium sulphate is far more effective in quenching flame than is water alone.

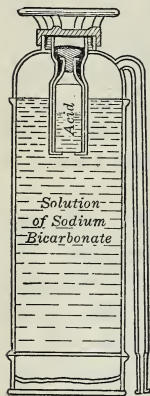
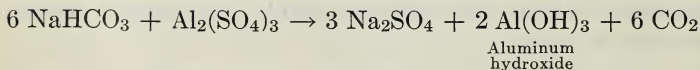


Fig. 89. Fire extinguisher.

The **foamite** system of fire protection, which is especially efficacious in extinguishing oil fires, produces on the burning surface a cover of carbon-dioxide foam which excludes air from the combustion. The carbon dioxide is formed by the union at the nozzle of the apparatus of two solutions of aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3$, and sodium hydrogen carbonate:

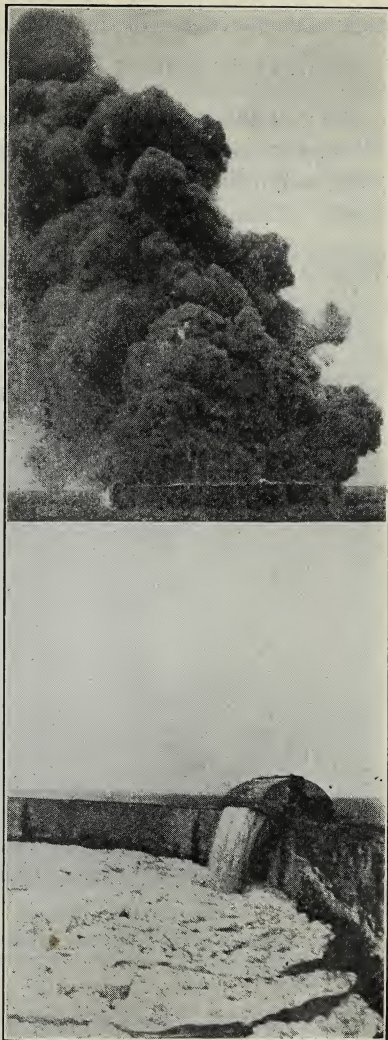


The sodium hydrogen carbonate solution carries also "*foamite*," a substance derived from licorice root. The aluminum hydroxide forms with the foamite a viscous fluid which the carbon dioxide blows into a tough, durable foam, effectively blanketing the burning surface.

167. Baking powders. Baking powder is a mixture of sodium hydrogen carbonate with a solid substance, feebly acid

in character, that will interact with the sodium hydrogen carbonate when water is added to yield carbon dioxide. In the dry mixture no change occurs, because the molecules of these two substances are not really in contact, being separated by a very thin film of air. When water is added, both constituents of the baking powder dissolve in it, perfect contact of the two kinds of molecules is then brought about, and the chemical change at once begins. All baking powders contain sodium hydrogen carbonate. According to the nature of the acid substance used along with it, we may distinguish three classes of baking powders:

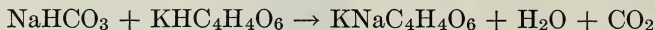
1. In the "cream-of-tartar" powders, the sodium hydrogen carbonate is mixed with *cream of tartar*, which is *potassium hydrogen tartrate*, $\text{KHC}_4\text{H}_4\text{O}_6$. When this mixture comes in con-



Courtesy of the Foamite Firefoam Co.

Fig. 90. Foamite extinguishing an oil fire.

tact with the water in the dough, the reaction is as follows:



2. A “**phosphate**” powder is a mixture of sodium hydrogen carbonate with *calcium hydrogen phosphate*, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, commonly sold at soda fountains under the name “*acid phosphate*.” The reaction is:



3. The “**alum**” powders contain *aluminum sulphate*, $\text{Al}_2(\text{SO}_4)_3$, which liberates carbon dioxide from the sodium hydrogen carbonate according to the equation given in the preceding section. The alum powders are cheaper than the others, and probably less wholesome.

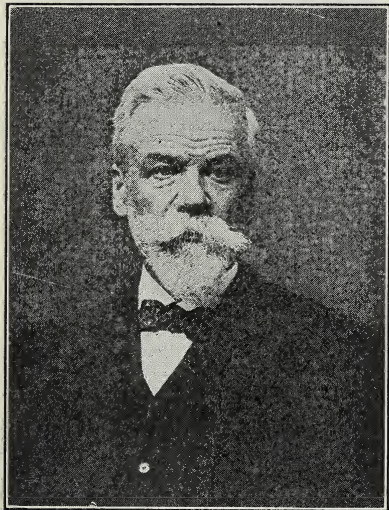


FIG. 91. ERNEST SOLVAY (1839-).

Belgian chemist; developed the process for obtaining sodium carbonate directly from sodium chloride.

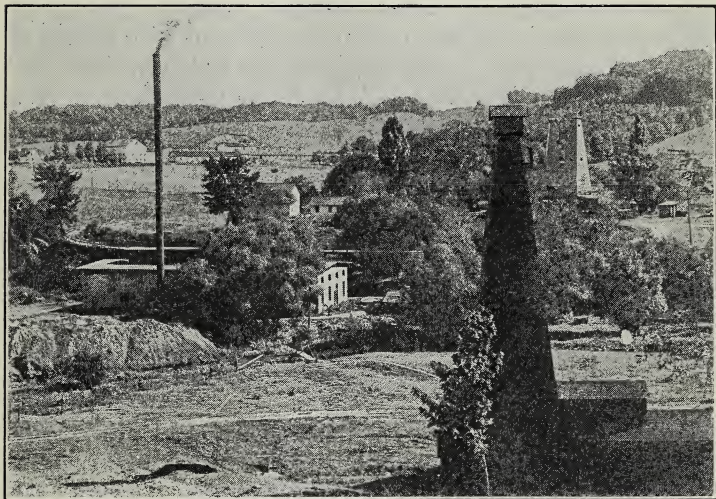
of sodium carbonate are made yearly from sodium chloride by the **Solvay process**, which was perfected by the Belgian chemist, *Ernest Solvay*, in 1863. The process is worked on

In addition to the two active substances, all baking powders contain a little corn starch, which improves their keeping qualities. The phosphate powders are by far the most important. Alum powders and cream-of-tartar powders scarcely appear on the market at present.

168. The Solvay process. About 2 million tons

a large scale at Syracuse, New York, the raw material being brine obtained from salt wells.

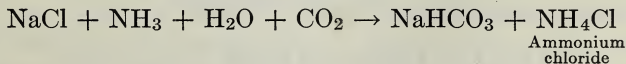
Ammonia gas, NH_3 , is passed into a concentrated salt solution contained in a closed iron kettle until the liquid will dissolve no more of the gas. The brine, saturated with ammonia, is then transferred to a tall iron tower, 30 m. high, fitted with a number of perforated shelves. Carbon dioxide is



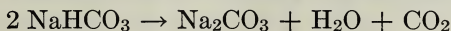
Courtesy of the Solvay Process Co.

Fig. 92. Salt wells of the Solvay Process Co. near Syracuse, New York.

passed in at the bottom of the tower under pressure. Sodium hydrogen carbonate is formed, separates upon the shelves as a white "sludge," and later falls to the bottom of the tower:



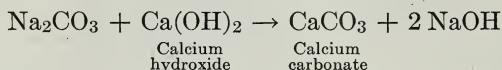
The sodium hydrogen carbonate is dried and heated gently in a revolving iron cylinder to convert it into sodium carbonate:



The carbon dioxide given off from this cylinder is collected and forced into the bottom of the tower just mentioned. The ammonia is recovered from the liquid left in the tower and used again.

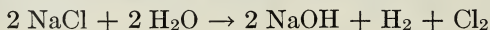
169. Sodium hydroxide, NaOH. Sodium hydroxide is a white, crystalline, deliquescent solid, which is about twice as dense as water, and which melts at about 300° C. It often appears in commerce in sticks, which are made by casting the melted substance. It dissolves in less than its own weight of water. The solution, which has a soapy feel, has a marked disintegrating action on animal and vegetable tissues. For this reason sodium hydroxide is often called **caustic soda**. In the household it is used for cleansing purposes under the name **lye**.

Sodium hydroxide is made by boiling a solution of sodium carbonate in an iron vessel with slaked lime, which is *calcium hydroxide*, Ca(OH)_2 :



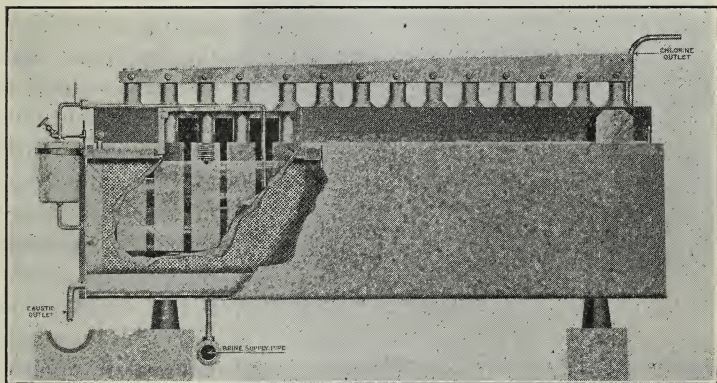
Since the calcium carbonate is insoluble in water, it is easily removed by allowing it to settle to the bottom of the liquid. The clear solution of sodium hydroxide is then drawn off and evaporated to dryness in an iron pan. Melted sodium hydroxide remains, which can be cast into sticks. Usually, however, it is allowed to solidify, crushed, and the coarse powder packed in tight iron drums for sale.

Large quantities of sodium hydroxide are also made by the electrolysis of a solution of sodium chloride:



The chlorine escapes at the anode, while the hydrogen and sodium hydroxide are formed at the cathode. The chief problem of the process is to keep the chlorine and sodium

hydroxide from coming into contact, which would result in the loss of both. In one of the many cells in use the anode is in one chamber and the cathode in another. The two chambers are separated by a porous partition of asbestos cloth or some similar material. This, being saturated with salt solution, allows the electric current to pass, but does not permit the chlorine to penetrate from the anode into the cathode chamber.



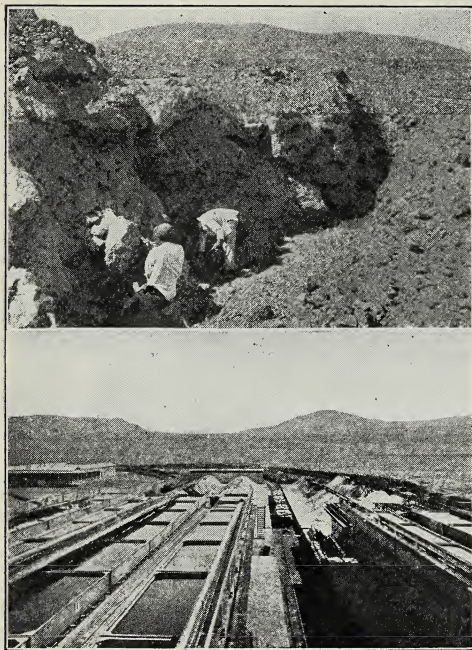
Courtesy of H. R. Nelson.

Fig. 93. The Nelson chlorine-caustic soda cell, a large installation of which is illustrated in Figure 70.

The electrolysis of salt solution is, as we have seen (§ 111), the process used for the industrial preparation of chlorine, of which sodium hydroxide is a by-product.

The largest use of sodium hydroxide is in the manufacture of soap, which is made by boiling a solution of sodium hydroxide with an animal or vegetable oil or fat. Another important application is in "mercerizing" cotton goods. The cloth, stretched in a frame, is dipped into a concentrated solution of sodium hydroxide. After washing and pressing, the fabric acquires a beautiful silky lustre and is stronger than before the treatment.

170. Sodium nitrate, NaNO_3 . Sodium nitrate occurs in a deposit 2 miles wide and 220 miles long, in the province of Tarapaca, a rainless region in northern Chile, between the Andes and the Pacific. The deposit, which is called *caliche*, is found in beds about a meter thick, gray, brown, or yellow in color, and containing from 10 to 65 per cent of sodium nitrate.



Courtesy of W. R. Grace & Co.

Fig. 94. Caliche mining and sodium nitrate refining in Chile.

The fact that sodium nitrate is quite soluble in water, while most of the impurities of the *caliche* are insoluble, makes it possible to purify it in a simple manner. The mineral is treated in iron boxes with boiling water. When the earthy impurities have settled, the clear solution of sodium nitrate is drawn off into another vessel and allowed to cool, whereupon the so-

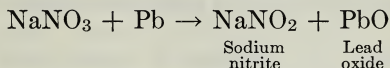
dium nitrate crystallizes. This product, which contains about 95 per cent of pure sodium nitrate, is shipped to the United States and to Europe.

The first cargo of Chilean sodium nitrate, often called "Chile saltpeter," was brought from the Tarapaca beds to

Europe in 1825. It found no purchaser, and it was finally thrown into the sea as worthless. At present it is being exported at the rate of $2\frac{1}{2}$ million tons annually, the greater part of which goes to the United States. It is employed in the manufacture of nitric acid, of sulphuric acid, and of potassium nitrate. It is one of the raw materials of the glass industry. It is also largely used as a fertilizer, to supply nitrogen to crops. Because of its solubility in water sodium nitrate would be washed out of the soil and lost if applied in the autumn. It is used, therefore, in the spring, after the crop is started.

Pure sodium nitrate forms colorless crystals which resemble cubes in appearance although in reality the angles are oblique. In trade it is often called "**nitrate of soda.**" It melts easily and is very soluble in water.

171. Sodium nitrite, NaNO_2 . Sodium nitrite is made by melting sodium nitrate with lead:



Sodium nitrite forms pale-yellow crystals which are much used in the manufacture of dyestuffs.

172. Sodium silicate, Na_2SiO_3 . Sodium silicate is a transparent, massive substance which resembles ordinary glass but differs from it in being soluble in water. It is commonly called "**water glass.**" Sodium silicate is made by melting sand with sodium carbonate. The product is usually boiled with water, which dissolves it, and is sold as a solution, which is used for fireproofing wood and cloth, as a cement, as an addition to cheap soaps, and for preserving eggs.

173. Sodium cyanide, NaCN . Sodium cyanide appears in commerce in the form of thin plates. It smells like bitter almonds and is intensely poisonous. A solution of sodium cyanide dissolves gold, and it is extensively used in extracting native gold from its ores in what is known as the *cyanide process* (§ 351).

SUMMARY

Sodium, though it does not occur native, is an abundant rock-forming element. It is obtained by the electrolysis of melted sodium hydroxide. It is a soft metal, intensely active, and slightly lighter than water, which rapidly interacts with it, forming hydrogen and sodium hydroxide.

Sodium chloride, NaCl , common salt, is the most abundant sodium compound. It is obtained by mining and by evaporating the water of salt springs, salt lakes, and the ocean.

Sodium sulphate, Na_2SO_4 , is made by the action of sulphuric acid on sodium chloride, hydrochloric acid being obtained as a by-product.

Sodium hydrogen carbonate, NaHCO_3 , commonly called **baking soda**, results when a solution of sodium chloride is saturated first with ammonia and then with carbon dioxide. When gently heated, it passes into sodium carbonate, Na_2CO_3 , which is a chemical product of great importance used in many industries.

Baking powders are mixtures of baking soda with weakly acid solids (cream of tartar, calcium hydrogen phosphate, or alum) which act upon the baking soda in presence of water, liberating carbon dioxide.

Sodium hydroxide, NaOH , commonly called **caustic soda**, is made by boiling a solution of sodium carbonate with slaked lime. It is also obtained by the electrolysis of a solution of sodium chloride.

Sodium nitrate, NaNO_3 , is found in abundance in the desert region of northern Chile. It is of great importance as a fertilizer and as a raw material for the manufacture of nitric acid and of potassium nitrate.

About 60 of the elements are **metals**. The metals are highly opaque, have a metallic lustre, and are more or less ductile, malleable, and tenacious. During electrolysis the metals move to the **cathode**.

Twenty of the elements are **non-metals**, which do not possess the physical properties of the metals. During electrolysis the non-metals appear at the **anode**.

The **light metals** are those of which the specific gravity is less than 5. They are less ductile, malleable, and tenacious than the **heavy metals**, and far more active chemically. With the exception of aluminum only the heavy metals are fitted for structural purposes.

EXERCISES

1. What changes occur when a piece of sodium is left exposed to the air?
2. Describe two methods of making sodium hydroxide.
3. What are the uses of sodium hydroxide in the household?
4. What industries are based, directly or indirectly, upon salt? Why?
5. When table salt becomes moist, what is the usual explanation? At the seashore even pure salt becomes wet. Why?
6. Describe three different sources of salt.
7. Make a tabular comparison of sodium carbonate and sodium hydrogen carbonate. Devise a test to distinguish the one from the other.
8. What is the difference between a *metal* and a *non-metal*? Between a *base* and a *noble metal*? Between a *light* and a *heavy metal*? If the light metals had been known during the Middle Ages, would they have been classed as base or noble?
9. How is sodium peroxide made? What is it used for? Why?
10. If sodium sulphite crystals are offered at 30 cents per pound and anhydrous sodium sulphite at 40 cents per pound, which is the better purchase? Why?
11. What is an *antichlor*?
12. Why is finished paper likely to contain a little sodium sulphite or sodium thiosulphate?
13. Explain the chemical fire extinguisher. Why is the stream thrown by it superior to water? What is *foamite*?
14. Describe the Solvay process for making sodium carbonate.
15. How is *caliche* purified for export?
16. How can sodium nitrate be converted into sodium nitrite?

17. How many metals are there among the elements? How many non-metals? What are the two liquid elements?

18. How many liters of hydrogen are formed by the action of 3 grams of sodium on water?

19. How many grams of sodium can be obtained by the electrolysis of 20 grams of sodium hydroxide?

20. How many liters of carbon dioxide are produced from 42 grams of sodium hydrogen carbonate (*a*) by heating; (*b*) by the action of sulphuric acid?

21. How many grams of sodium hydroxide can be made by boiling 53 grams of sodium carbonate with slaked lime? How many grams of slaked lime should be used?

22. On a hot summer day some workmen who had just shovelled a pile of dry powdered sodium carbonate were employed in unloading with shovels a car of dry lime. Painful sores developed upon the exposed portions of the skin. Explain. How could the accident have been prevented? Would the error have been as dangerous in winter? Why?

23. Why is there no chemical change in baking powder until water is added.

CHAPTER XVIII

POTASSIUM (K = 39)

174. Potassium and sodium. Potassium resembles sodium closely, and the corresponding compounds of the two are so similar that for most purposes the one can be substituted for the other. Most of the compounds of both metals are white, crystalline solids, freely soluble in water. The potassium compound is usually less soluble than the corresponding sodium compound, it crystallizes better, and is, therefore, more easily purified. The sodium compounds are cheaper and for this reason are used in place of the potassium compounds whenever possible.

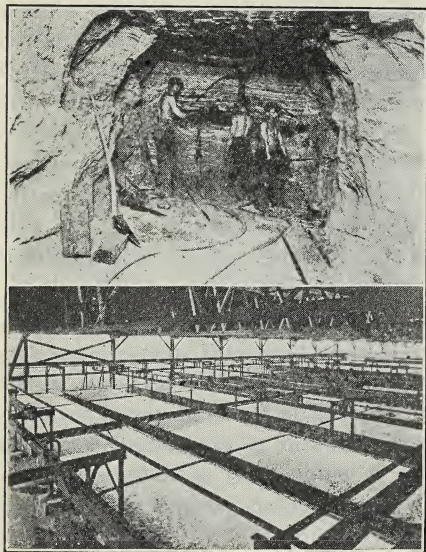
175. Occurrence of potassium. Potassium does not occur native, but in combination it is an abundant rock-forming element, making up nearly 2.5 per cent of the solid crust of the earth. The two abundant minerals *felspar* and *mica* are potassium compounds, so that the amount of potassium locked up in the rocks is unlimited. A cubic yard of average granite contains 250 lb. of potassium; a cubic yard of felspar contains 800 lb.

At Stassfurt in northern Germany there occurs a large deposit of potassium minerals, most of which are soluble in water. The bed is 300 m. thick and contains 30 different minerals, most of which are compounds containing *potassium chloride*, KCl , or *potassium sulphate*, K_2SO_4 . A similar extensive deposit is found in the French province of Alsace.

176. Sources of potash. The term "potash" is applied commercially to impure, inexpensive grades of potassium chloride, sulphate, or carbonate, suitable for use in preparing fertilizers. Prior to the outbreak of the World War in 1914 the

United States imported all of its potash from Germany, the imports being valued at \$15,000,000 annually. When this supply was cut off, there was for a time great activity in the direction of establishing a domestic supply, but without much permanent success. Several industries could furnish potash as a by-product. Among these are the beet-sugar industry, the washing of wool, the manufacture of Portland cement, and

the smelting of iron ores in the blast furnace. In the dry regions of western Nebraska and California there are lakes from the water of which potassium chloride or sulphate can be obtained by evaporation. The water of these lakes is the most important domestic source of potash. Certain giant sea weeds of our Pacific coast contain, when dried, one-third of their weight of potassium chloride, but the manufacture of potash from them is



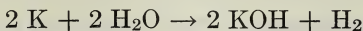
Courtesy of La Société des Potasses d'Alsace.

Fig. 95. Mining and refining potash in Alsace.

too costly to compete with other methods. Wood ashes, which contain *potassium carbonate* up to 10 per cent of their weight, can be used directly on the soil as a fertilizer.

177. Properties of potassium. Potassium is made by the electrolysis of melted potassium hydroxide, the method being the same as that used in obtaining sodium (§ 148). Like sodium, potassium is a white, waxy metal which oxidizes

rapidly in the air. Its specific gravity is 0.86. It interacts with water more rapidly than does sodium:



Potassium
hydroxide

As a rule the interaction of sodium and water runs to an end without the appearance of flame, but when potassium is dropped into water, the hydrogen at once takes fire. Potassium itself or any of its compounds colors the flame of the Bunsen burner a delicate *lilac*. This flame color serves as a *test* for potassium and its compounds. Potassium has had no industrial applications of importance.

The *alloy* of potassium and sodium is a liquid which resembles mercury in appearance.

178. Flame tests. Like sodium and potassium, many other metals produce characteristic colors when they, or their compounds, are placed in the faint blue flame of the Bunsen burner. Some of the more important of these colors are the following:

Element	Flame Color
Sodium	Yellow
Potassium	Lilac
Lithium	Crimson
Calcium	Orange
Strontium	Red
Barium	Green

These **flame tests**, as they are called, are serviceable in detecting the metals in question, but difficulties arise in analyzing mixtures in which several metals are present together. A typical case of this kind would be a powder consisting of a large percentage of sodium chloride with small percentages of the chlorides of the other five elements in the list above. Such a mixture, when introduced into the flame, would seem to produce merely an intense yellow color due to the sodium, and the detection of the other metals present by simple inspection

would be impossible. Evidently, some way of sorting out into its constituent colors the complex light radiated by the flame is necessary.

179. The spectroscope. This sorting out is precisely what takes place when light passes through a glass prism. In

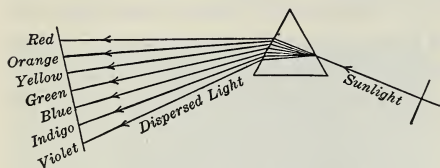


Fig. 96. Analysis of sunlight by the prism.

Figure 96 a beam of sunlight, admitted into a dark chamber by means of a slit in the shutter, falls upon a prism and proceeds thence to a sheet tacked to the wall.

The result shows that all the rays of light are *refracted*, or bent out of their original course, this bending being *downward* if the prism is placed with its edge *upward* as in the diagram.

The *violet rays*, which are those having the shortest wave length, are refracted the most and appear lowest upon the screen,

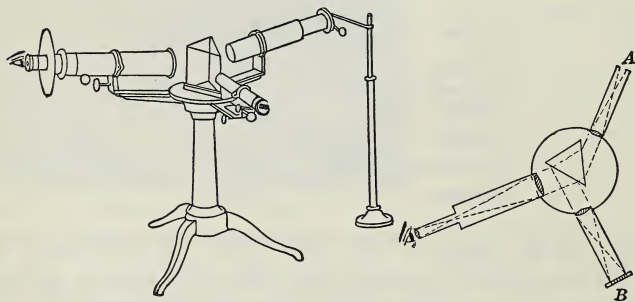


Fig. 97. The spectroscope.

while the *red rays*, those of longest wave-length, deviate least from their original direction and take the uppermost position. The other colors arrange themselves between these two extremes, so that we obtain, counting from above downward, a series of bands of color in this order: violet, indigo, blue, green, yellow,

orange, and red. This is called the solar **spectrum**. The most familiar instance of the spectrum is the *rainbow*.

The application of this property of the prism to chemical analysis is shown in Figure 97, which represents the **spectroscope**. The substance to be analyzed is held in a flame at *A* by means of a loop of platinum wire, which must be absolutely clean. The light passes through a narrow slit into the *collimator*, a tube containing lenses that make the rays parallel, and thence to a prism. The spectrum which issues from the prism is examined through a second tube, which is really a small telescope. Into this tube also is reflected the image of a graduated scale carried in the third tube at *B*.

In the spectroscope the presence of sodium is indicated by two bright yellow lines quite close together. By means of the instrument the millionth part of a gram of sodium can be detected with certainty even when it is mixed with other elements.

When a mixture of the chlorides of sodium, potassium, and lithium is heated, the yellow sodium lines appear, while the presence of potassium is shown by a dark red line at one end of the spectrum and a violet line at the other. At the same time, the lithium produces a bright red band and a pale yellow line.

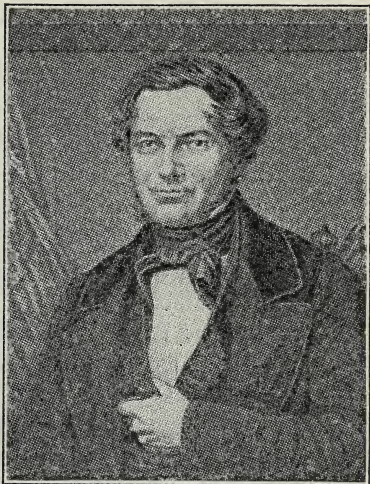


FIG. 98. ROBERT WILHELM BUNSEN
(1811-1899).

German chemist, professor of chemistry in the University of Heidelberg; invented the Bunsen burner, photometer, spectroscope, and other apparatus; discovered, with Kirchhoff, spectrum analysis and, by this means, the elements caesium and rubidium.

Thus all three metals can be identified without risk of mistake. A colored plate of various spectra is given in the frontispiece to this book.

COMPOUNDS OF POTASSIUM

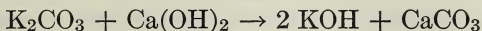
180. Potassium chloride, KCl , and potassium sulphate, K_2SO_4 , form white, anhydrous crystals, freely soluble in water. Both are important constituents of fertilizers. Farmers prefer the sulphate to the chloride, claiming that it gives better results in use. Potassium chloride and sulphate are also employed in the manufacture of other potassium compounds.

Potassium bromide, KBr , and potassium iodide, KI , form white, cubical, anhydrous crystals, very soluble in water. Both are of the utmost importance in medicine and photography.

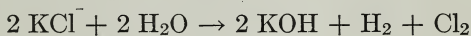
181. Potassium carbonate, K_2CO_3 . Potassium carbonate can be obtained from wood ashes and as a by-product of the wool and beet-sugar industries. To prepare potassium carbonate from wood ashes the ashes obtained by burning waste wood, such as stumps, twigs and sawdust, are placed in a tank with a perforated bottom. Boiling water is poured through, which dissolves the potassium carbonate. The liquid which filters through is evaporated to dryness in an iron pot, when impure potassium carbonate remains as a dark mass, which becomes white when heated to redness in a furnace. Elm, maple, and birch give a larger yield than the other woods. Potassium carbonate is also prepared from potassium chloride and from potassium sulphate. It is a white, deliquescent powder which dissolves in its own weight of cold water. Impure grades of potassium carbonate are sold under the name of "**pearlash**." Potassium carbonate finds application in soap making. It is also used in the manufacture of plate glass, crown glass, and flint glass.

182. Potassium hydroxide, KOH . Potassium hydroxide is called "**caustic potash**" in commerce on account of the intense disintegrating action of its solution on animal and

vegetable matter. It is obtained by methods precisely similar to those which yield sodium hydroxide, for instance, by boiling a solution of potassium carbonate with calcium hydroxide (slaked lime):



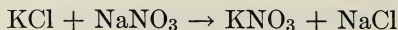
The clear solution of the potassium hydroxide is poured off from the insoluble calcium carbonate and boiled down until the water is evaporated and melted potassium hydroxide remains, which is then cast into sticks. Potassium hydroxide is also obtained, in the same way as sodium hydroxide, by electrolysis, potassium chloride being substituted for sodium chloride. The same type of cell is used (§ 169). Chlorine is liberated at the anode, while in the cathode chamber hydrogen and potassium hydroxide solution are formed:



Potassium hydroxide is a brittle, white, deliquescent solid, which closely resembles sodium hydroxide. When exposed to the air it absorbs carbon dioxide and passes into potassium carbonate. It is used in the preparation of shaving soap, cold cream, soft soap, and lubricating compounds.

183. Potassium nitrate, KNO_3 . In India, Persia, and Egypt deposits of *potassium nitrate* are found, impregnating the soil in the neighborhood of large cities. In such localities decaying animal matter containing nitrogen is abundant. When this oxidizes in contact with the potassium compounds always present in the soil, potassium nitrate is formed, its presence being indicated by a white incrustation upon the surface. It can be obtained by extracting the earth in large tubs with hot water and allowing the clear filtered solution to crystallize. The potassium nitrate prepared in this way is chiefly used in the manufacture of the best grades of black gunpowder.

Potassium nitrate is also made by heating a mixture of potassium chloride and sodium nitrate with a limited amount of water in an iron vessel:



The sodium chloride separates in crystals in the boiling liquid and is fished out with a perforated ladle or removed by straining the liquid through canvas. When the clear solution, freed from sodium chloride, is allowed to cool, the potassium nitrate crystallizes.

Potassium nitrate forms long, grooved, colorless, anhydrous crystals, which melt readily and dissolve in less than half their weight of boiling water. It contains nearly half its weight of oxygen. A cubic centimeter of potassium nitrate contains as much oxygen as 2,700 c.c. of air. At a high temperature, therefore, it is a vigorous oxidizing agent. When potassium nitrate is sprinkled on a coal fire, a great increase in the energy of the combustion occurs. Finely powdered mixtures of potassium nitrate with combustibles like sulphur, charcoal, rosin, or shellac burn with explosive violence.

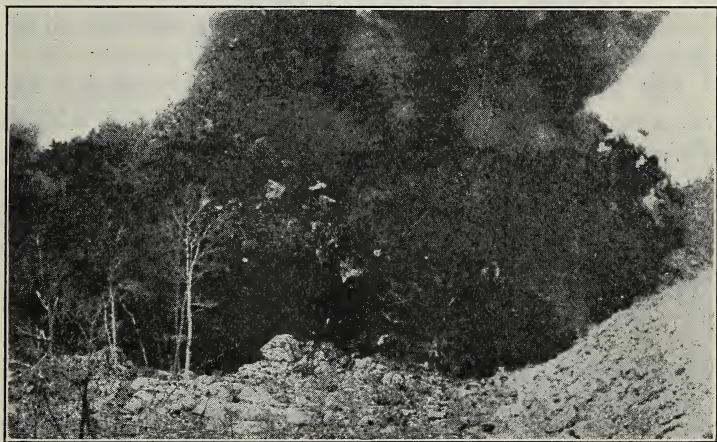
Potassium nitrate is often called "**nitre**," or "**saltpeter**." It is applied in the preservation of meats, especially "corned" beef, and in the manufacture of fuses and fireworks. Its largest use is in the production of black gunpowder.

184. Black gunpowder. The old black powder, which burns with a dense smoke, is an intimate mixture containing by weight 6 parts of potassium nitrate, 1 part of sulphur, and 1 part of charcoal. These materials are powdered separately in rotating drums containing bronze balls. They are then mixed, moistened, and transferred for final pulverizing to a grinding mill which is operated electrically from a distance, on account of the possibility of explosion.

The powdered mass is next pressed hydraulically into a sheet which looks like slate. The sheet is broken up and the fragments sieved to obtain uniform size of grain. The powder

is finally dried and polished in a rotating wooden drum, in which graphite is added at the end to form a lustrous film on the surface of the grains. After sifting to remove dust, the powder is packed in air-tight containers for market.

Charcoal made from well seasoned willow wood is preferred for gunpowder. Black gunpowder, though obsolete as a propelling charge for guns in warfare, is made in larger quantities

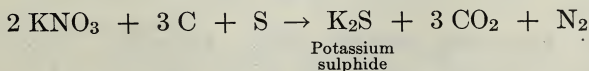


Courtesy of the Bureau of Mines.

Fig. 99. A large blast of black powder, a chemical reaction on a grand scale depending upon rapidity for its effectiveness.

than ever before. It is used in mining and quarrying, in ammunition for hunting, in saluting charges, and in shrapnel shells.

We may write a simple equation for the explosion of gunpowder thus:

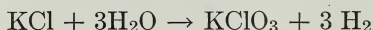


The chemistry of the explosion is really quite complex, but this equation will help us to remember that the oxygen of the

potassium nitrate oxidizes the carbon, while the nitrogen is evolved as a gas. In fact, the sudden formation of gas is the cause of the explosion, since the powder, in a small fraction of a second, expands to several thousand times its original volume.

A pound of good coal produces 13 times as much heat when burned as does a pound of gunpowder. No explosive contains anything like as much energy in the same weight as does gasoline or kerosene. The effects of explosives are due to the *quickness* with which the energy is set free rather than to the total amount available.

185. Potassium chlorate, KClO_3 . Potassium chlorate, like potassium hydroxide, is made by the electrolysis of a solution of potassium chloride, but the process is carried out in a different way. The liquid is warm, there is no diaphragm, and during the electrolysis the contents of the cell are stirred to mix the products at the anode and cathode. The potassium chlorate separates in crystals while the current is passing:



Potassium chlorate forms flat, white, four-sided crystals which contain no water of crystallization. It melts easily. When heated above its melting-point, it gives off oxygen and passes into potassium chloride. It is used in fireworks (especially in colored fires), as a constituent of explosives, and in the manufacture of safety matches. A solution of potassium chlorate is sometimes prescribed in medicine as a gargle in cases of sore throat. It is poisonous, however, and must not be swallowed. Potassium chlorate is a frequent constituent of patent medicines and lozenges that are sold for the relief of colds, but the wisdom of taking it internally is open to serious question.

186. Potassium cyanide, KCN . Potassium cyanide is a white solid which smells like bitter almonds and is highly poisonous. Like sodium cyanide, it is employed in electroplating and in the extraction of gold from its ores.

SUMMARY

Potassium is very similar to sodium, and the corresponding compounds of the two elements resemble each other closely.

Most of the compounds of potassium are white solids, freely soluble in water.

The characteristic colors produced in the Bunsen flame by many metals and their compounds offer convenient **flame tests** for the detection of these metals.

By means of the **spectroscope** the light of a complex flame can be analyzed into the characteristic **spectra** of the elements composing it.

Potassium chloride and **potassium sulphate** are of great importance as fertilizers.

Wood ashes contain **potassium carbonate** and are placed on the soil to supply potassium to plants.

Potassium nitrate is often called "saltpeter" or "niter."

Black gunpowder is a mixture of potassium nitrate with charcoal and sulphur.

Potassium chlorate is the substance from which oxygen is obtained in the laboratory. It is used in the manufacture of explosives, fireworks, and matches, and in medicine.

EXERCISES

1. Give two methods of distinguishing potassium from sodium.
2. Is potassium a light or a heavy metal? Is it suitable for constructive purposes? Why?
3. What is "*potash*"? What are its uses? Previous to 1914 where did the United States obtain its potash?
4. Mention seven possible domestic sources of potash. What is the chief domestic source?
5. How are nitrates formed in the soil? What is the importance of this formation? Why does a field often improve in fertility if simply allowed to remain uncropped for a time?
6. Sodium chloride is cheaper than potassium chloride, but sup-

posing the two sold at the same price, which would be the more suitable material for making chlorine by electrolysis? Why?

7. How would you proceed if given a cord of maple wood and required to convert its "potash" into sticks of potassium hydroxide?

8. How is potassium chloride electrolyzed (*a*) to obtain chlorine and potassium hydroxide; (*b*) to obtain potassium chlorate?

9. Why is potassium hydroxide called "caustic potash"? Should sticks of caustic potash or caustic soda be handled with the fingers?

10. What is the immediate and what the final result of exposing potassium hydroxide to the air?

11. Calculate the percentage composition of potassium nitrate.

12. How many kilograms of potassium nitrate can be made from a metric ton of sodium nitrate, and how many kilograms of potassium chloride must be used? A metric ton is 1,000 kg.

13. How many grams of potassium are required to liberate from water enough hydrogen to combine with 3 grams of oxygen to form water?

14. How many liters of oxygen are needed to form water with the hydrogen given off by the action of 9.75 grams of potassium upon water?

REVIEW QUESTIONS

1. What is the law of multiple proportions? In what way does the atomic theory explain it?

2. Explain how to calculate from the formula of hydrogen chloride (*a*) the percentage composition; (*b*) the weight of 1 liter; (*c*) the volume of 1 gram; (*d*) the specific gravity referred to oxygen; (*e*) the specific gravity referred to air.

CHAPTER XIX

VALENCE; ACIDS, BASES, AND SALTS; CHEMICAL NOMENCLATURE

VALENCE

187. Combining power. The following list contains the names and formulas of some of the more important compounds of hydrogen with other elements:

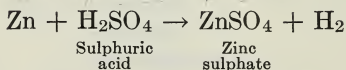
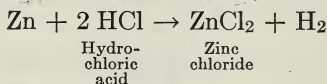
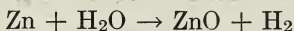
Element	Name of Compound	Formula
Chlorine.....	Hydrogen chloride	HCl
Oxygen.....	Water	H ₂ O
Sulphur.....	Hydrogen sulphide	H ₂ S
Nitrogen.....	Ammonia	NH ₃
Carbon.....	Methane	CH ₄

Both chlorine and oxygen unite with hydrogen with explosive energy, but, although the atom of chlorine combines with but 1 hydrogen atom, that of oxygen combines with 2. Hence the oxygen atom has twice the combining power of the chlorine atom.

The combining power of the atoms is called **valence**. The *unit* of valence is the combining power of the atom of hydrogen. Thus, chlorine, which combines with hydrogen atom to atom, has a valence of 1, or is *univalent*, whereas oxygen, the atom of which is able to hold 2 hydrogen atoms, has a valence of 2, or is *bivalent*. From the formula of ammonia, NH₃, it is clear that nitrogen has a valence of 3, or is *trivalent*. The simplest compound of carbon and hydrogen, *methane*, has the formula CH₄,

from which it follows that the atom of carbon has 4 times the combining power of the atom of hydrogen, and that carbon is *quadrivalent*. No higher valence than 4 is known in hydrogen compounds.

188. Valence of the metals. Thus, the number of atoms of hydrogen that are held in combination by 1 atom of another element measures the valence of that element. But most of the *metals* do not combine with hydrogen at all, and for them some other method of determining the valence must be devised. *The valence of a metal is the number of hydrogen atoms which 1 atom of the metal is able to replace in a chemical change.* For example, zinc does not combine with hydrogen, but it displaces hydrogen from many hydrogen compounds, as in the following reactions:



In these cases the zinc atom substitutes itself for 2 atoms of hydrogen. Since 1 zinc atom always takes the place of 2 atoms of hydrogen when zinc displaces hydrogen from a hydrogen compound, it follows that zinc is *bivalent*. Most of the common metals are bivalent. *Sodium, potassium, and silver are univalent, and aluminum is trivalent.*

189. Valence of radicals. A group of atoms that exists in the molecule of a compound and is transferred unbroken in chemical changes to the molecules of other compounds is called a **radical**. Thus, the group SO_4 is found in combination with 2 atoms of hydrogen in sulphuric acid, H_2SO_4 , and passes over unchanged into the molecules of sulphates like ZnSO_4 , Na_2SO_4 , etc. Like a single atom, a radical has a definite valence. SO_4

is the radical of sulphuric acid, and from the formula H_2SO_4 it is clear that the radical is *bivalent*. The formula of nitric acid, HNO_3 , shows that the nitric-acid radical, NO_3 , is *univalent*, whereas in phosphoric acid, H_3PO_4 , the radical PO_4 must be *trivalent* since it is combined with 3 atoms of hydrogen.

190. Utility of valence. Valence is of great importance as an aid in remembering and writing chemical formulas. When two elements combine, the total number of units of valence of each element entering into combination must be the same. Thus, chlorine is univalent, and so is potassium; therefore, the two unite atom to atom, and the formula of *potassium chloride* is KCl . Oxygen, however, is bivalent, so that it takes 2 atoms of potassium to satisfy 1 of oxygen, and the formula of *potassium oxide* is K_2O . The radical NO_3 of nitric acid is univalent. One atom of potassium will satisfy it, and the formula of *potassium nitrate* is KNO_3 . But the bivalent radical SO_4 will require 2 potassium atoms, and *potassium sulphate* must have the formula K_2SO_4 . For similar reasons the formula of *potassium phosphate* must be K_3PO_4 .

Since zinc is bivalent, its atom combines with 2 chlorine atoms, forming *zinc chloride*, ZnCl_2 . For the same reason, an atom of zinc will combine with 2 NO_3 radicals in *zinc nitrate*, $\text{Zn}(\text{NO}_3)_2$. Oxygen, which, like zinc, is bivalent, will unite with it atom to atom to form *zinc oxide*, ZnO . The formula of *zinc sulphate* will be ZnSO_4 , because both the zinc atom and the SO_4 radical possess 2 units of valence. With the trivalent PO_4 radical, the only resource is to take 3 Zn to 2 PO_4 , and the formula of *zinc phosphate* becomes $\text{Zn}_3(\text{PO}_4)_2$.

In the case of the trivalent metal aluminum the chloride will have the formula AlCl_3 , and the nitrate will be $\text{Al}(\text{NO}_3)_3$. With the oxide we have the same problem as with zinc phosphate. Its formula must be Al_2O_3 . For similar reasons the formula of *aluminum sulphate* must be $\text{Al}_2(\text{SO}_4)_3$. *Aluminum phosphate* will be simply AlPO_4 , since there are 3 units of valence on each side. All the formulas just worked out have

been tested by actual analysis of the substances and found to be correct.

The results obtained will now be collected into a brief table for reference. The formulas are typical. Any other metals or radicals of the same valence might be used, and the formulas would be similar. The compounds of the quadrivalent metal *thorium* have been added.

TYPICAL FORMULAS BASED ON KNOWN VALENCES

Compound	Univalent Metal <i>Potassium</i>	Bivalent Metal <i>Zinc</i>	Trivalent Metal <i>Aluminum</i>	Quadrivalent Metal <i>Thorium</i>
Chloride.....	KCl	ZnCl ₂	AlCl ₃	ThCl ₄
Nitrate.....	KNO ₃	Zn(NO ₃) ₂	Al(NO ₃) ₃	Th(NO ₃) ₄
Oxide.....	K ₂ O	ZnO	Al ₂ O ₃	ThO ₂
Sulphate.....	K ₂ SO ₄	ZnSO ₄	Al ₂ (SO ₄) ₃	Th(SO ₄) ₂
Phosphate....	K ₃ PO ₄	Zn ₃ (PO ₄) ₂	AlPO ₄	Th ₃ (PO ₄) ₄

Valences higher than 4 are not common among compounds of practical importance. The highest valence that has been established is 8.

191. Variable valence. The valence of some elements varies in different compounds. Thus, mercury forms a chloride HgCl, in which the mercury atom is univalent, and another chloride HgCl₂, in which the mercury atom is bivalent. Corresponding to the chloride HgCl is a whole series of compounds—oxide, nitrate, sulphate, etc.—in which the mercury is univalent, and corresponding to HgCl₂ is another series of compounds in which the mercury is bivalent. Similarly, iron may be bivalent or trivalent, tin may have a valence of 2 or 4, and some other elements behave in the same way. In such cases we must know beforehand which valence the atom exerts and write the formula accordingly.

ACIDS, BASES, AND SALTS

192. Acids. Hydrochloric acid is a member of a large and important class of substances—the **acids**.

Acids, when dilute, have the *sour taste* familiar in vinegar or lemon juice.

When concentrated, many of them have a *caustic action* on the skin or on other animal or plant substance.

Litmus, which is a blue dye derived from a species of lichen, is turned *red* by acids.

Acids are hydrogen compounds. The hydrogen in them is combined either with a *single atom of a non-metal*, as in the case of HCl , or with a radical composed of non-metallic atoms, as in HNO_3 , H_2SO_4 , and H_3PO_4 .

The non-metals are, therefore, the acid-forming elements.

When an acid interacts with a metal, the hydrogen escapes, and the metal atom takes its place in the molecule, forming a product called a **salt**.

Acids may be solids, liquids, or gases, but *their characteristic properties only appear when they are dissolved in water*.

In the industries sulphuric acid is the most important acid.

193. Bases. Sodium hydroxide, NaOH , and potassium hydroxide, KOH , are types of another important class of substances, the **bases**, which are directly opposed in their properties to the acids.

Bases have a bitter, nauseous, metallic taste, and their concentrated solutions disintegrate the skin and other animal tissues; hence the names “caustic soda” and “caustic potash” for sodium hydroxide and potassium hydroxide, respectively.

Litmus that has been reddened by an acid is again turned *blue* by bases.

Bases are hydroxides. The name **hydroxyl** is given to the radical OH which is present in all bases. In most bases the hydroxyl is in combination with an atom of a metal, as in

NaOH and KOH. Thus, *the metals are the base-forming elements.*

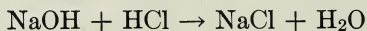
Most bases are *solids*. They are always employed in solution in water, and it is only in that condition that their characteristic properties appear.

In the industries sodium hydroxide is the most important base. Calcium hydroxide (slaked lime) is the cheapest base and is widely used, but its slight solubility in water unfits it for many purposes.

The term **alkali** is often used with the same meaning as "base," and a substance that turns red litmus blue is said to have an **alkaline reaction**.

194. Salts. When a solution of sodium hydroxide is mixed with hydrochloric acid in the proportion of exactly 1 molecular weight of each, the liquid becomes warm, showing that a chemical change has occurred. The sour taste of the acid and the bitter taste of the sodium hydroxide disappear, and the liquid tastes like salt water. It has no effect on the color of either red or blue litmus. Evaporation to dryness leaves a white residue of sodium chloride, NaCl.

The only possible conclusion is that sodium hydroxide and hydrochloric acid interact according to the following equation:

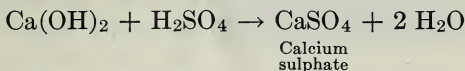
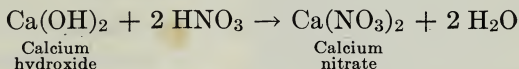
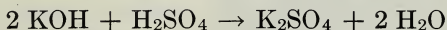
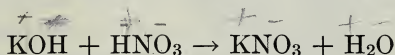


Sodium chloride is a type of a third important class of substances—the **salts**. Solutions of the salts have a **saline** taste, quite different from the sour taste of the acids and the bitter flavor of the bases. A pure solution of a salt, free from acid or base, has *no effect* upon the color of either red or blue litmus.

The *formula* of a salt is obtained by substituting a *metal*, or a *radical* that behaves like a metal, for hydrogen in the formula of the corresponding acid. The formulas HCl and NaCl furnish a typical instance. In the same way the formula of the potassium salt of nitric acid, HNO₃, will be KNO₃. Atten-

tion must be paid to the valence of the metal atoms and of the acid radicals. Thus, to take the place of both hydrogen atoms in sulphuric acid, H_2SO_4 , 2 univalent atoms of potassium will be required, so that the formula of potassium sulphate is K_2SO_4 . But 1 atom of a bivalent element like calcium can replace both hydrogen atoms, and the formula of calcium sulphate is CaSO_4 .

When an acid and a base are brought together, *water* and the *salt* corresponding to the metal of the base and the radical of the acid are produced. The chemical change that occurs is called neutralization. We have just examined a typical instance in the interaction of sodium hydroxide and hydrochloric acid. The following are additional examples; the student will notice the necessity of attending to the rules of valence:



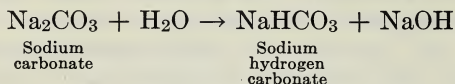
Because of their great chemical activity, acids and bases rarely occur in the crust of the earth. Salts are much less active and are abundant as minerals.

Salts differ more in their properties than do acids and bases. It is not always possible, therefore, to substitute one salt for another in practical work, even when the two are closely related chemically. Sodium chloride and sodium nitrate are perhaps the most essential salts as raw materials in the industries, but many other salts, as we shall see, are of very great importance.

195. Hydrolysis. Solutions of salts like sodium chloride and sodium nitrate, in which both the acid and the basic con-

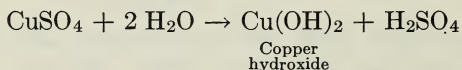
stituents are very active, have no effect upon the color of either red or blue litmus. They are said to be **neutral**. But a solution of *sodium carbonate*, even when dilute, has a strong *alkaline* reaction, turning red litmus blue as though sodium hydroxide were present.

As a matter of fact, the solution *does* contain sodium hydroxide. When sodium carbonate is dissolved, some of it interacts with the water, yielding sodium hydrogen carbonate and sodium hydroxide:



The presence of a small proportion of sodium hydroxide in the liquid accounts for the alkaline reaction, the soapy feel, and the cleansing power of a solution of sodium carbonate (washing soda).

On the other hand, copper sulphate, CuSO_4 , dissolves in water to form a solution which behaves as though an *acid* were present, coloring blue litmus *red*. The cause is similar. The liquid contains sulphuric acid, produced by the interaction of a small proportion of the copper sulphate with water:



The term **hydrolysis** is applied to this interaction of salts with the water in which they are dissolved. When a salt solution reacts acid or alkaline to litmus, we may regard it as a proof that a portion of the salt has interacted with the water, liberating an active acid or an active base, as the case may be. A salt like sodium carbonate, which contains an *active base* with an *inactive acid*, will react *alkaline*, while a salt like copper sulphate, which contains an *inactive base* with an *active acid*, will react *acid*.

THE NAMES OF ELEMENTS AND COMPOUNDS

196. The elements. Elements that occur native or that can be very easily obtained from minerals containing them were known to the ancients. Such are copper, silver, gold, lead, iron, and sulphur. The names of elements like these are usually different in different languages, because in all countries they are simply parts of the familiar daily language of the people.

The elements isolated since chemistry became a science have been named by their discoverers, who have usually assigned to the *metals* names ending in **-ium** and to the *non-metals* names ending in **-ine**. Such names are uniform, or nearly so, in all languages. No general principle has guided the discoverer in the naming of the elements. *Columbium*, *gallium*, and *germanium* were named for patriotic reasons; *aluminium*, now more generally called *aluminum*, because it is a constituent of *alum*; *sodium* because it is the metal of *soda*; *radium* in allusion to the rays which it sends forth; *chlorine* for its green color and *iodine* on account of its beautiful purple vapor; while the term *bromine* refers to the intolerable odor of the element.

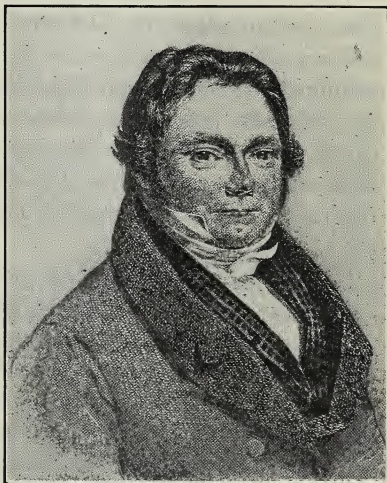


FIG. 100. JOHANN JACOB BERZELIUS
(1779-1848).

Swedish chemist, professor of chemical pharmacy at Stockholm; discovered several elements, determined atomic weights, and developed electrochemical theory; introduced our present system of chemical symbols and chemical nomenclature.

197. Compounds of two elements. A compound of two elements only is called a *binary* compound. The system followed in naming binary compounds can be illustrated by the case of common salt.

The compounds of chlorine with the metals, taken as a class, are called the *chlorides*, and each particular chloride is indicated by prefixing the name of the corresponding metal, used as an adjective. In this manner is derived the name *sodium chloride*, which means a substance composed wholly of sodium and chlorine, no third element being present. Hydrogen chloride, potassium chloride, and silver chloride are other examples. In the same way the compounds of *sulphur* with the metals are called the *sulphides*, forming a class of which the members are copper sulphide, lead sulphide, mercury sulphide, etc.

Thus, chemical names are not arbitrary, but are so chosen as to express, as far as possible, the *composition* of the substance.

The names of binary compounds end in -ide. This termination is added to a characteristic portion of the name of the non-metal, and the word thus produced forms the second portion of the name, the name of the metal going first as an adjective.

When there are several compounds of the same two elements, some way of distinguishing them from each other must be devised. In such cases the syllable **per-** is often prefixed to the second word of the name of that compound which contains a higher percentage of the non-metal than does the other. For example:

Barium oxide.....	BaO	Lead oxide.....	PbO
Barium peroxide	BaO ₂	Lead peroxide	PbO ₂

Another plan is to distinguish the two compounds by adding the suffix **-ous** or **-ic** to the *first word* of the name. The compound that contains *less* of the *non-metal* receives the suffix **-ous**, and the compound that contains *more* of the *non-metal* receives the suffix **-ic**. Examples are:

	-ous Compounds	-ic Compounds
<i>Mercury</i> {	Mercurous chloride... HgCl Mercurous oxide..... Hg_2O	Mercuric chloride... HgCl_2 Mercuric oxide..... HgO
<i>Iron</i> {	Ferrous chloride..... FeCl_2 Ferrous oxide..... FeO	Ferric chloride..... FeCl_3 Ferric oxide..... Fe_2O_3
<i>Tin</i> {	Stannous chloride.... SnCl_2 Stannous oxide..... SnO	Stannic chloride.... SnCl_4 Stannic oxide..... SnO_2

An inspection of the table will show that the termination **-ic** applies to that compound in which the metal atom exerts the *higher valence*.

A third possibility is to distinguish the compounds by numerical prefixes to the second word of the name. For example:

Carbon monoxide CO	Carbon dioxide CO_2
Manganese monoxide MnO	Manganese dioxide MnO_2
Nitrogen trioxide N_2O_3	Nitrogen pentoxide N_2O_5

198. Ternary compounds. A *ternary compound* contains, in addition to the metal and the non-metal, a third element, which in practically all cases studied in high-school work is *oxygen*. The presence of the oxygen is indicated by the termination **-te**. For example:

Binary Compound	Ternary Compound
Potassium chloride KCl	Potassium chlorate KClO_3
Sodium sulphide Na_2S	Sodium sulphite Na_2SO_3
Zinc sulphide ZnS	Zinc sulphate ZnSO_4

199. Acids, bases, and salts. A *binary acid* is named like other binary compounds, for example:

Hydrogen chloride..... HCl	Hydrogen bromide..... HBr
Hydrogen iodide..... HI	

These acids are gases which are chiefly employed in water solutions. To these solutions, respectively, are given the names *hydrochloric acid*, *hydrobromic acid*, and *hydriodic acid*. Here the prefix **hydro-** indicates a binary compound of hydrogen.

The other important acids are ternary compounds containing *oxygen*. The important oxygen acid formed by an element

receives the termination **-ic** as in chloric acid, HClO_3 , and sulphuric acid, H_2SO_4 , and the names of the salts end in **-ate**.

If the same element forms a second acid containing *less* oxygen, its name is made to terminate in **-ous**, while the names of the salts end in **-ite**. For example:

Acid		Salt	
Sulphuric acid.....	H_2SO_4	Sodium sulphate.....	Na_2SO_4
Sulphurous acid.....	H_2SO_3	Sodium sulphite.....	Na_2SO_3
Chloric acid.....	HClO_3	Potassium chlorate.....	KClO_3
Chlorous acid.....	HClO_2	Potassium chlorite.....	KClO_2

SUMMARY

The **valence** of an atom is measured by the number of atoms of hydrogen with which it combines, or of which it can take the place.

A group of atoms that exists in a series of related compounds is called a **radical**. Radicals, like single atoms, have a definite valence.

Valence is of the utmost assistance in writing formulas and equations.

Some of the properties of acids, bases, and salts are summarized in the following table:

	Acids	Bases	Salts
TASTE	Sour	Bitter	Saline
EFFECT ON LITMUS	Blue to red	Red to blue	None (usually)
PHYSICAL STATE	Solid, liquid, or gas	Solid	Solid
CHEMICAL CONDUCT	Active	Active	Less active
OCCURRENCE IN NATURE	Rare	Rare	Common
MOLECULAR STRUCTURE	Hydrogen, combined with non-metal atom or radical	Hydroxide of metal atom or radical	Acid, with hydrogen replaced by metal or radical

Neutralization is the interaction of an acid with a base, yielding water and a salt.

Hydrolysis is the interaction of a small proportion of a salt with water when dissolved. It occurs (1) when the acid is inactive; (2) when the base is inactive. In (1) the active base produced will make the liquid alkaline to litmus; in (2) the active acid liberated will make the liquid acid to litmus.

The **metals** are **base-forming** elements.

The **non-metals** are **acid-forming** elements.

Binary compounds contain **two elements only**. The second, or non-metallic, term in the name of a binary compound ends in **-ide**.

Ternary compounds contain **three elements**, one of which is usually oxygen.

The most important oxygen acid of an element receives the termination **-ic**, and the names of its salts end in **-ate**.

If there is a *second* oxygen acid containing *less oxygen*, its name terminates in **-ous** and the names of its salts in **-ite**.

EXERCISES

1. What is the valence of carbon in *carbon tetrachloride*, CCl_4 ? In *carbon dioxide*, CO_2 ?

2. Taking the hydrogen atoms as univalent, what are the valences of the zinc and of the carbon in zinc methyl, $\text{Zn}(\text{CH}_3)_2$?

3. What are the valences of the sulphur, phosphorus, and platinum in sulphur trioxide (SO_3), phosphorus pentoxide (P_2O_5), and platinum tetrachloride (PtCl_4)?

4. If gold chloride has the formula AuCl_3 , what is the formula of the corresponding oxide?

5. Silver, calcium, and chromium have valences of 1, 2, and 3, respectively. Write the formulas of the chlorides, nitrates, oxides, sulphates, and phosphates of these metals.

6. In the *stannous* compounds tin is *bivalent*, and in the *stannic* compounds it is *quadrivalent*. Write the names and formulas of the chlorides, oxides, sulphates, and phosphates.

7. In the sulphides sulphur is *bivalent*. Write the formulas of the sulphides of silver, calcium, zinc, aluminum, chromium, gold, platinum, and thorium.

8. Among the non-chemical public the idea is universal that all acids are liquids. How much truth is there in this opinion?

9. The name *oxyger* means acid-producer, and it was given to the element because it was supposed to be contained in all acids. Was this opinion correct?

10. In old textbooks carbon dioxide (CO_2) is called *carbonic acid*, and sulphur dioxide (SO_2), *sulphurous acid*. Criticize these antiquated names.

11. The rare non-metal *selenium* forms an acid which resembles sulphuric acid and is called selenic acid, H_2SeO_4 . Write the names and formulas of the salts of this acid with sodium, potassium, silver, calcium, zinc, aluminum, chromium, and thorium.

12. Make a tabular comparison of the properties of hydrochloric acid, sodium hydroxide, and sodium chloride.

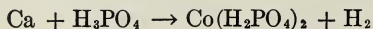
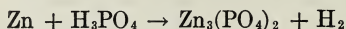
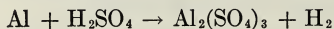
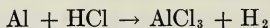
13. What is the characteristic radical of bases? Define *alkali* and *alkaline*.

14. What difference in composition is indicated by the following pairs of names: nitrous acid and nitric acid; sodium nitrate and sodium nitrite; potassium sulphate and potassium sulphite; sulphuric acid and sulphurous acid; mercurous chloride and mercuric chloride. Write the formulas of all the compounds named.

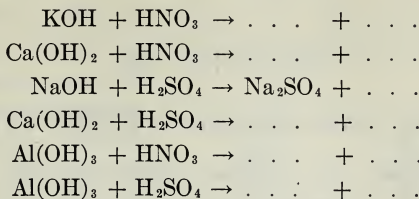
15. What is meant by *binary* and *ternary* compounds? How are they named?

16. What is the cause of the alkaline reaction and cleansing power of a solution of washing soda? Account for the fact that copper-sulphate solution reddens blue litmus paper.

17. Supply (on paper, not in the textbook) the missing coefficients in the following:



18. Complete (on paper, not in the textbook) the following, supplying coefficients where necessary:



19. How many grams of nitric acid are needed to convert 400 grams of potassium hydroxide into potassium nitrate?

20. 10 grams of pure sodium hydroxide are dissolved in water. (a) How many grams of pure nitric acid must be added to make the solution neutral? (b) How many grams of sodium nitrate would be obtained if this were done?

21. I have a solution that contains just 40 grams of pure sodium hydroxide in 1 liter. Calculate the quantities by weight of (a) HCl, (b) HNO₃, and (c) H₂SO₄ that will be required to neutralize 1 c.c. of it.

22. 15.25 grams of nitric acid and 23.25 grams of sodium hydroxide are dissolved in water and mixed. What two solutes does the solution contain, and how many grams of each? Do not calculate *water*.

23. 50 grams of sodium hydroxide are dissolved in water and the solution mixed with enough hydrochloric acid to contain 50 grams of hydrogen chloride. What solutes and how many grams of each are contained in the resulting liquid? Do not calculate *water*.

REVIEW QUESTIONS

1. Define *substance*, *element*, *compound*, *mixture*, *atom*, *molecule*, and *molecular weight*.

2. What is Avogadro's Hypothesis? How is it applied in determining molecular weights?

3. Write an algebraic equation that expresses the relation between the molecular weight of a gas and its specific gravity referred to air.

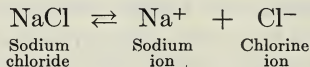
4. Describe the electrolysis of water (a) in the laboratory, (b) on a large scale.

CHAPTER XX

IONIZATION; IONS OF ACIDS, BASES, AND SALTS

200. Ionization. In a water solution of sugar, the sugar separates into its individual molecules, which are distributed uniformly through those of the water. When sodium chloride dissolves in water, the disintegration goes even further, for the sodium-chloride molecule itself is broken up, the atoms of sodium and of chlorine are torn apart, and each moves about independently in the liquid. Moreover, each atom receives an electric charge when the salt dissolves, the sodium atom being charged positively, and the chlorine atom negatively.

This separation of the molecules of dissolved substances into charged atoms (or charged radicals) is called **ionization**, and the charged atoms (or charged radicals) are called **ions**. The equation may be written:



The *plus* and *minus* signs above and to the right of the atoms indicate their electric charges. Since the solution as a whole is electrically *neutral*, these charges must be *equal*. The double arrow signifies that ionization is *reversible*. If, for example, the water be removed by evaporation, the atoms again unite, the opposite charges neutralize each other, and solid sodium chloride, which is composed of the molecules NaCl, remains.

The disruption of the molecule into electrically charged fragments by mere solution in water is a startling idea, which seems, at first sight, quite improbable. Let us, therefore, examine the evidence on which it is founded. This is so conclusive that ionization is now accepted by all chemists.

201. The conducting power of solutions. A simple apparatus for investigating the conducting power of solutions for the electric current is shown in Figure 101. The liquid to be tested is placed in a beaker and the platinum electrodes dipped into it. The current may be taken from a *direct-current* lighting circuit. The lamp interposes a suitable resistance and, at the same time, indicates, by lighting up more or less, whether the solution allows much or little current to pass.

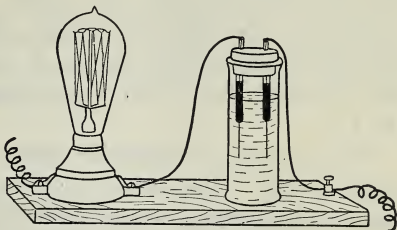


Fig. 101. Apparatus for investigating conducting power of solutions.

Results of experiments with solutions of different substances show that compounds may be divided according to the conductivity of their solutions into two very different classes:

1. Those of which solutions in water *conduct* the electric current. This class includes *all acids, bases, and salts*. Solutions of *active acids*, like hydrochloric acid, and of *active bases*, like sodium hydroxide, conduct well. Solutions of *inactive acids*, like acetic acid, and of *inactive bases*, like ammonium hydroxide (NH_4OH), conduct badly.

2. Those of which solutions in water are *non-conductors*. This class includes all those numerous substances which are *not* acids, bases, or salts, such as sugar, glucose, alcohol, ether, glycerine, etc.

Compounds of which aqueous solutions conduct the electric current are called **electrolytes**. All acids, bases, and salts are electrolytes.

Compounds of which aqueous solutions are non-conductors are called **non-electrolytes**. The non-electrolytes include all of the countless thousands of compounds that are not acids, bases, or salts. They are far more numerous than the electrolytes.

202. The lowering of the freezing point. A sugar solution freezes at a lower temperature than does pure water, for the reason that the attraction of the sugar molecules for the water molecules must be overcome before the latter can separate from the solution in the form of ice. The formula of sugar is $C_{12}H_{22}O_{11}$; its molecular weight, therefore, is 342. A gram-molecular-weight (342 grams) of sugar, when dissolved in a liter of water, will lower the freezing point of the water by $1.9^{\circ}C$.

The formula of alcohol, C_2H_6O , shows that its molecular weight is 46. A gram-molecular-weight of alcohol (46 grams) dissolved in a liter of water lowers the freezing point by $1.9^{\circ}C$., precisely the same effect as that produced by a gram-molecular-weight of sugar. A large number of experiments of this kind with different compounds has resulted in the following general law:

A gram-molecular-weight of any non-electrolyte will lower the freezing point of a liter of water $1.9^{\circ}C$.

Since the gram-molecular-weights of different substances contain the same number of molecules, this result indicates that the extent of the lowering of the freezing point depends solely upon the *number* of the molecules of the solute. The *nature* of the solute, provided that it is a *non-electrolyte*, is without influence upon the result.

203. The freezing points of conducting solutions. A solution of sodium chloride gives a very different result. A gram-molecular-weight (58.5 grams) of sodium chloride dissolved in a liter of water produces a lowering of the freezing point almost *twice as great* as the result obtained with a gram-molecular-weight of sugar, alcohol, and other substances of which the solutions are non-conductors.

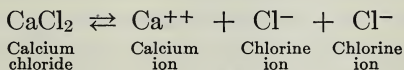
This can mean only that there are twice as many particles of solute in the sodium-chloride solution as in the sugar solution. From this it follows that each molecule of sodium chloride has separated into a sodium *ion* and a chlorine *ion*, which

move about independently in the liquid and produce a doubled lowering of the freezing point.

Other compounds that separate into 2 ions behave like sodium chloride. Thus, a gram-molecular-weight of pure HCl, when dissolved in a liter of water, gives about double the lowering of the freezing point produced by a gram-molecular-weight of a non-electrolyte. This proves ionization of the hydrogen chloride according to the equation:



Compounds of which the molecules cleave into 2 ions never give more than *twice* the theoretical lowering of the freezing point. But the molecules of many substances break up into 3 ions. *Calcium chloride* is an example. Two chlorine ions are formed, while the single calcium ion takes up a double positive charge:



In agreement with this we find that a gram-molecular-weight of calcium chloride dissolved in a liter of water gives about *three times* the lowering of the freezing point produced by a gram-molecular-weight of sugar or of any other non-electrolyte.

204. The rise in the boiling point. A solution of sugar boils at a higher temperature than water, because the sugar molecules attract the water molecules and make it more difficult for them to leave the liquid in the form of steam. When a gram-molecular-weight of sugar (342 grams) is dissolved in a liter of water, the solution boils at 100.52° C., a rise in the boiling point of 0.52° C. Precisely the same result is obtained with any other *non-electrolyte*. Thus, the molecular weight of glucose, C₆H₁₂O₆, is 180, and 180 grams of glucose dissolved in a liter of water yields a solution which boils at 100.52° C.

A gram-molecular-weight of any non-electrolyte dissolved in a liter of water raises the boiling point by 0.52°C .

On the other hand, when a gram-molecular-weight of sodium chloride (58.5 grams) is dissolved in a liter of water, the solution boils at about 101°C ., so that the sodium chloride raises the boiling point about twice as much as does the equivalent quantity of sugar. The molecular weight of potassium chloride, KCl , is 74.5, and 74.5 grams of it gives the same result as does a gram-molecular-weight of sodium chloride, raising the boiling point of a liter of water to about 101°C . Finally, a gram-molecular-weight of a substance like calcium chloride, CaCl_2 , of which the molecule cleaves into 3 ions, raises the boiling point of a liter of water by about 1.5° , or nearly three times as much as does the equivalent quantity of sugar.

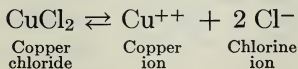
In general, then, when one gram-molecular-weight of a solid is dissolved in a liter of water:

1. If there is no ionization, so that a non-conducting solution is formed, the rise in the boiling point will be 0.52°C .
2. If each molecule of the solute separates into 2 ions, the rise in the boiling point will be about $0.52^{\circ}\text{C} \times 2$.
3. If each molecule of the solute separates into 3 ions, the rise in the boiling point will be about $0.52^{\circ}\text{C} \times 3$.

We have seen that these three statements apply also to the lowering of the freezing point if we everywhere substitute 1.9°C . for 0.52°C . The most convincing proof of ionization is found in these facts. On the one hand we have a class of compounds, of which sodium chloride is a type, which show, when dissolved and tested by the two methods just discussed, that each molecule in solution has broken up into 2 or more fragments. On the other hand we have a class of compounds, of which sodium chloride is again the type, which show, by the way in which their solutions conduct the electric current, that these solutions contain positively and negatively charged atoms which carry the current from one electrode to the other.

Now these two classes are identical. Acids, bases, and salts are the only compounds that show when dissolved, by their excessive effects upon the boiling point and freezing point of water, that their molecules have broken into fragments. Acids, bases, and salts are also the only compounds that show, when dissolved in water, by the ability of the solutions to conduct the electric current, that these solutions must contain positively and negatively charged atoms or radicals instead of molecules.

205. Electrolysis. The passage of electricity through metals produces no permanent change in them, as is shown by the fact that in the electric wiring system of the household the same copper wire can be used for an indefinite time. But, as we have seen in the electrolysis of sodium-chloride solution, the transfer of electricity through a *solution* causes chemical decomposition, the products of which appear at the positive and negative electrodes, where the electricity enters and leaves the liquid. Thus, copper chloride (CuCl_2) dissolves freely in water. Ionization takes place, as is shown by the fact that the lowering of the freezing point and the rise in the boiling point are far greater than when the equivalent quantity of sugar is dissolved. Since twice as many chlorine ions as copper ions are formed, the copper ion must take up a positive charge equivalent to the negative charges on 2 chlorine ions, so that we can write the equation for the ionization of copper chloride thus:



When the greenish-blue solution is placed in the apparatus of Figure 101 and the electric current passed, chlorine bubbles up from the anode, while the cathode becomes plated with copper. This behavior is typical of that of the soluble compounds of the heavy metals. When their solutions are electrolyzed, the *metal* is liberated at the *cathode*. Thus, in elec-

troplating with copper, nickel, silver, or gold, the object to be plated is placed in a solution containing a suitable compound of the metal desired in the coating and connected with the *cathode*. If the compound undergoing electrolysis contains only 1 *non-metal* in union with the metal, the non-metal, as in

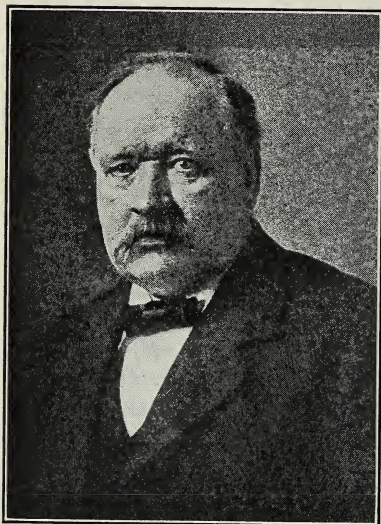


FIG. 102. SVANTE AUGUST ARRHENIUS (1859-).

Swedish chemist, director of the Physico-Chemical Department of the Nobel Institute; advanced in 1887 the modern theory of dissociation and ionization in electrolytes.

the case of copper chloride, will be liberated at the *anode*. Whereas if the metal is combined with a *radical*, as in *copper sulphate*, CuSO_4 , the occurrences at the anode are more complex.

Like the chemical elements, *electricity is composed of atoms*. The atom of electricity, which is called the **electron**, is very much smaller than the other atoms, for it weighs only $\frac{1}{1786}$ as much as the atom of hydrogen. Through the copper wiring of the household countless billions of electrons pass each second with little resistance, but a *solution* allows no *free* electrons to traverse it. Just as a

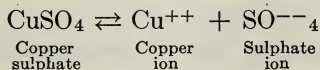
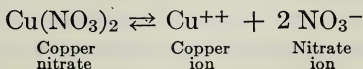
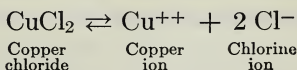
traveller who comes to a river where there is no bridge must take a boat, so electricity, upon arriving at the gap between the electrodes, is stopped completely unless there are charged atoms (*ions*) in the liquid to carry it. Thus, in the electrolysis of copper chloride the chlorine ions (Cl^-), with their negative charges, are attracted by the positive charge on the anode and

move slowly to it. When they reach it, they lose their negative charges and unite in pairs to form molecules of chlorine gas, Cl_2 , which is thus set free at the anode.

On the other hand, the blue copper ions (Cu^{++}), with their positive charges, are attracted to the cathode, which removes the charges, converting the blue ions, which are very soluble in water, into ordinary red copper metal, which is insoluble in water and plates the cathode.

In the electrolysis of sodium-chloride solution the chlorine ions behave at the anode just as they do in the electrolysis of copper chloride. At the cathode sodium cannot appear as a plating on account of the presence of water, with which, as the student will recall, it interacts with explosive violence. We may assume that as soon as the sodium ion gives up its charge to the cathode and becomes an ordinary atom of sodium, it interacts with the water present, producing hydrogen, which escapes, and sodium hydroxide, which dissolves. The products, therefore, are, at the anode, chlorine gas, and at the cathode, hydrogen gas and sodium-hydroxide solution.

206. Further evidence of ionization. Let us examine the equations for the ionization of three familiar compounds of copper:



If these substances existed in solution in unbroken molecules, just as sugar does, the *colors* of the three solutions should be different, since each would contain a very different kind of molecule. But if they ionize according to the scheme given

above, the colors of the three solutions should be identical, for they are all colored only by the presence of the copper ion, all three negative ions being colorless. The fact is that the three dilute solutions have a greenish-blue color which is *precisely the same* in all. The same statement applies to salts of other metals the ions of which possess a color. Thus, the salts of *nickel*, when dissolved in water, possess a grass-green color which is the same for all. Similar statements are true of all solutions containing the ions of the same color—a most interesting proof of ionization.

It is a remarkable fact that the *tests* by means of which we detect with such certainty the presence of the metals in solutions work equally well no matter from what salt of the metal the solution is made. Thus, a very delicate and serviceable test for copper is the addition of *ammonia*, which produces a deep blue color in an aqueous liquid in which copper is present; the test gives equally good results on solutions made up with copper chloride, copper nitrate, copper sulphate, or any other salt of the metal.

Here again ionization gives the explanation. The test is for the copper *ion* and therefore applies to any solution containing it. The negative ions, like the water molecules, are not concerned in the chemical change that causes the characteristic blue color.

207. Ions of acids and bases. All *acids* are hydrogen compounds, but there are innumerable hydrogen compounds, such as water, alcohol, and glycerine, that are not acids. In order to be an acid, a compound when dissolved in water must ionize with formation of *hydrogen ions*.

The hydrogen ion (H^+) is the characteristic ion of acids, and their sour taste, their effect upon litmus, and their action upon metals are all due to the hydrogen ions in the solution.

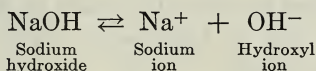
An active acid, like hydrochloric acid in water solution, is ionized almost completely. Hence the solution is a good conductor, for there are numerous positive and negative ions to carry

the electricity. For the same reason, hydrogen ions are numerous, and the acid properties which result from their presence are well developed.

When an inactive acid, like acetic acid, is dissolved in water, most of the molecules remain intact, only a small percentage being ionized. Hence the solution is a poor conductor, and the acid properties, on account of the relative scarcity of hydrogen ions, are feeble.

That the acid properties are really due to hydrogen ions can be directly proved by preparing a solution of pure, dry hydrogen-chloride gas in dry chloroform. In this case no ionization of the HCl molecules takes place, as is shown by the fact that the solution is a non-conductor of the electric current. It is devoid of acid properties, having, for instance, no action upon metals and no effect upon the color of blue litmus.

A base is a hydroxide which, when dissolved in water, ionizes with formation of *hydroxyl ions* (OH^-). For example:

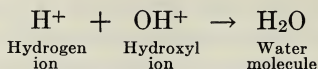


The hydroxyl ion is the characteristic ion of bases, and their bitter taste, their effect on litmus, and their caustic action on animal and vegetable matter are all due to the hydroxyl ions in the solution.

An active base, like sodium hydroxide, is one which, when dissolved in water, is ionized almost completely. Hence the solution is a good conductor of the electric current, and since hydroxyl ions are numerous in it, the basic properties are strongly marked.

An inactive base, like ammonium hydroxide, NH_4OH , has only 1 per cent or less of its molecules ionized when in water solution. Accordingly, the solution conducts badly, and the basic properties are weak.

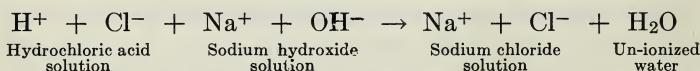
208. Neutralization. When a solution of an acid is mixed with a solution of a base, the hydrogen ions and the hydroxyl ions unite to form water:



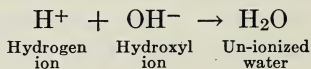
and, as we have seen, both the acid and basic properties vanish. *Neutralization is purely the affair of the hydrogen ions and the hydroxyl ions.* The negative ion of the acid and the positive ion (metal ion) of the base have nothing to do with it whatever.

Consider, for instance, the neutralization of hydrochloric acid, HCl, by sodium hydroxide, NaOH. The solution of hydrochloric acid contains H^+ and Cl^- , that of sodium hydroxide contains Na^+ and OH^- . After the two are mixed we have a solution of sodium chloride, NaCl, which contains Na^+ and Cl^- .

Thus, the sodium ions and the chlorine ions are in precisely the same state after the neutralization as they were before. All that has occurred has been the union of the hydrogen ions and the hydroxyl ions to form water. The equation brings out the point more clearly:



Evidently the sodium ion and the chlorine ion might as well be subtracted from both sides and the equation written simply:

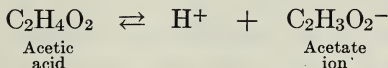
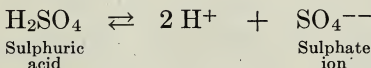
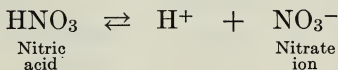
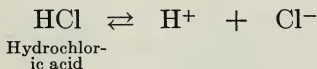


This explains a surprising fact which attracted the attention of chemists long before the discovery of ions. The *amount of heat* produced when a gram-molecular-weight of an active acid is neutralized by a gram-molecular-weight of an active

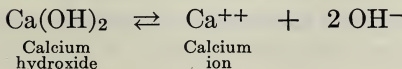
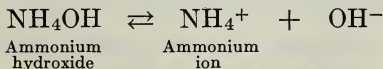
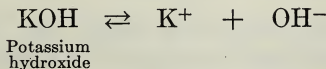
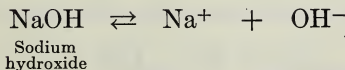
base is *always the same*, no matter what particular acid and base are used. The explanation is that each neutralization is merely the union of 1 gram of hydrogen ions with 17 grams of hydroxyl ions. Since nothing else happens, the acid and base employed have no influence on the amount of heat liberated, which is, therefore, always the same (13,700 calories).

209. Equations for ionization. The following equations will serve as examples of the way in which molecules break up into ions in solutions of some important acids, bases, and salts:

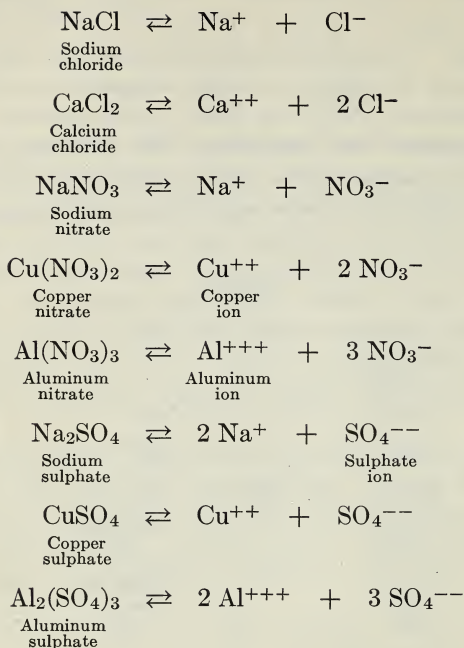
ACIDS



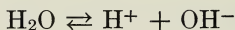
BASES



SALTS



210. The electrolysis of water. *Pure water* is ionized to a very small extent into hydrogen ions and hydroxyl ions:



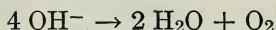
This cleavage into ions is so slight that the enormous volume of 10 million liters is required to contain 1 gram of hydrogen ion and the equivalent quantity (17 grams) of hydroxyl ion. To contain this mass of water would require a cubical tank 21.5 m. (over 23.5 yd.) in each dimension.

Since in pure water the number of ions H^+ and OH^- is so small in comparison with the number of molecules H_2O , the

liquid scarcely conducts the electric current. If we were to use pure water in the apparatus of Figure 39 (§ 65), hydrogen and oxygen would be liberated in time, but the action would be so slow that it would be impracticable to wait for it.

When sulphuric acid is added to the water in the apparatus, countless billions of hydrogen ions appear in the liquid and move to the cathode, where they lose their electric charges and are converted into ordinary hydrogen molecules H_2 . Accordingly, hydrogen gas escapes from the cathode.

The negative current is carried to the anode by the negative ions (SO_4^{--}) of the sulphuric-acid radical. When the anode is reached, there are present two kinds of negative ions struggling to be discharged, the SO_4^{--} ions and the OH^- ions which, as we have just seen, are present in pure water. The OH^- ions lose their charges far more easily than do the SO_4^{--} ions, so the OH^- ions are discharged:



and oxygen bubbles up from the anode. The SO_4^{--} ions, after transporting the electrons to the anode, suffer no further change, so that the quantity of sulphuric acid in the liquid remains the same. In this respect the electrolysis of water resembles catalytic action. It is the *sulphuric acid ions* that *carry the current*, but it is the *water* that is *decomposed*.

It remains only to inquire how the supply of hydrogen ions and hydroxyl ions is maintained, in spite of the fact that both are constantly being discharged. The answer is that water in all circumstances must contain 1 gram of hydrogen ion and 17 grams of hydroxyl ion in 10 million liters. As the discharge of the ions goes on, new molecules of water are ionized:



so that the concentrations of both ions is always maintained constant.

SUMMARY

Acids, bases, and salts when dissolved in water **conduct** the electric current. Aqueous solutions of substances that do not find a place in any of these three classes are **non-conductors**.

Taken together, acids, bases, and salts are called **electrolytes**.

Compounds like sugar and glycerine, which are not acids, bases, or salts, are called **non-electrolytes**.

When a non-electrolyte is dissolved in water, its molecules are merely dispersed uniformly through those of the water.

When an electrolyte is dissolved in water, **ionization** occurs. This means that some of the molecules of the electrolyte are broken up into positively and negatively charged fragments called **ions**.

An ion may be either a single atom or a radical.

The most important positive ions are the hydrogen ion (H^+), the ammonium ion (NH_4^+), and those of the metals.

The most important negative ions are the chlorine ion (Cl^-), the bromine ion (Br^-), the iodine ion (I^-), the fluorine ion (F^-), the hydroxyl ion (OH^-), the nitrate ion (NO_3^-), the sulphate ion (SO_4^{--}), and the phosphate ion (PO_4^{---}). Many other negative ions are known.

The ionization of **inactive** acids and bases is very **incomplete**. Hence their solutions are **poor conductors**.

Active acids and bases are ionized more **completely**, and their solutions are **good conductors**.

A gram-molecular-weight of any *non-electrolyte* dissolved in a liter of water raises the boiling point of the water $0.52^\circ C$. and lowers its freezing point $1.9^\circ C$.

Because of ionization, the *electrolytes* when dissolved in water affect the boiling point far more than do the non-electrolytes. A gram-molecular-weight of an electrolyte like sodium chloride, each molecule of which separates into 2 ions, raises the boiling point and lowers the freezing point of a liter of water twice as much as does a gram-molecular weight of a non-electrolyte. This is convincing evidence of ionization.

Another proof of ionization is the fact that *solutions con-*

taining the same colored ion all have the same color, without regard to the compound dissolved when the solution was made.

Further evidence of ionization is furnished by the fact that the *tests* for a given metal give the same results on all solutions containing the ions of that metal. The same statement applies to the tests for the negative ions of acids. Thus, the test for chlorine with silver nitrate gives the well-known curdy white precipitate of silver chloride, not only when a solution of silver nitrate is mixed with one of hydrochloric acid, but also when a solution of silver nitrate is added to a solution of any metallic chloride. Silver nitrate, therefore, is a *test for the chlorine ion*, not for any special chlorine compound.

The **hydrogen ion** (H^+) is characteristic of **acids** and causes their sour taste, effect on litmus, action on metals, etc.

The **hydroxyl ion** (OH^-) is characteristic of **bases** and occasions their bitter taste, effect on litmus, caustic action on animal and vegetable matter, etc.

Neutralization is the union of hydrogen ions with hydroxyl ions to form un-ionized water.

EXERCISES

1. Write equations for the ionization of the following compounds: potassium chloride, KCl ; potassium nitrate, KNO_3 ; lead nitrate, $Pb(NO_3)_2$; bismuth nitrate, $Bi(NO_3)_3$; thorium nitrate, $Th(NO_3)_4$; potassium sulphate, K_2SO_4 ; calcium sulphate, $CaSO_4$; aluminum sulphate, $Al_2(SO_4)_3$; thorium sulphate, $Th(SO_4)_2$.

2. What is the exact distinction between a sodium *atom* and a sodium *ion*? What difference in properties results?

3. Explain exactly what you understand by a chlorine *atom*, a chlorine *molecule*, and a chlorine *ion*.

4. What is an *electrolyte*? How could you find out whether a solution of washing soda were an electrolyte?

5. Dilute sulphuric acid attacks iron rapidly but concentrated sulphuric acid has little effect upon iron and is shipped in iron tank cars. Explain.

6. What are the chief properties (a) of hydrogen gas, (b) of hydrogen ions?

7. Anhydrous hydrogen chloride has no effect upon anhydrous sodium hydroxide. Why is this?

8. Explain exactly what happens (a) when sodium chloride is dissolved in water, (b) when an electric current is passed through the solution.

9. Would sea water be a better or a poorer conductor of the electric current than rain water? How would the freezing points of the two compare?

10. Explain what happens: (a) when hydrogen chloride is dissolved in water; (b) when sodium hydroxide is dissolved in water; (c) when the two solutions are mixed; (d) when the mixed solution is evaporated to dryness.

11. Explain the electrolysis of water. What part is played by the sulphuric acid?

12. Potassium chlorate ionizes thus: $\text{KClO}_3 \rightleftharpoons \text{K}^+ + \text{ClO}_3^-$. Explain the fact that a solution of silver nitrate gives no precipitate with a solution of potassium chlorate. Silver nitrate gives a precipitate, however, in a solution made by heating potassium chlorate to redness and dissolving the residue in water. Why?

13. State briefly the evidence for ionization that is obtained by a study of the boiling points and freezing points of solutions.

14. Distinguish clearly between the meanings of the two terms *ionization* and *electrolysis*.

15. In what way does a study of the colors of solutions furnish evidence of ionization?

16. Explain the fact that the neutralization of a gram-molecular-weight of any active acid by a gram-molecular-weight of any active base always liberates the same quantity of heat.

17. Suppose you were to find that a certain substance lowered the freezing point of water twice as much as did the equivalent quantity of sugar. What conclusion would you draw regarding the nature of the substance? What would you predict with respect to the electrical conductivity of the solution?

CHAPTER XXI

NITROGEN (N = 14)

211. Occurrence. *Free nitrogen* makes up nearly four-fifths (78 per cent) by volume of the atmosphere. The most abundant *nitrogen compound* in nature is *sodium nitrate*, NaNO_3 , the occurrence of which in vast deposits in Chile has already been described. The bodies of plants and animals are composed, to a large extent, of nitrogen compounds, which also constitute large percentages of many indispensable food products.

212. Nitrogen in chemical combination. The compounds of nitrogen are of great practical importance. Nitrogen is the characteristic element of *explosives*—all of the principal explosives are nitrogen compounds or mixtures containing them. A class of complex nitrogen compounds known as **proteins** forms the most essential constituent of *food*. Among food-stuffs rich in nitrogen compounds are poultry, lean meat, cheese, peas, and beans. Food products free from nitrogen, like sugar and cornstarch, may be wholesome, but they cannot alone sustain life.

On the whole, the foods rich in nitrogen are by far the most costly materials of the diet. An excess of such foods is not merely wasteful, but it may do serious damage by overburdening the organs that have to eliminate the nitrogen from the body. An excess of foods poor in nitrogen, which class includes bread, cereals, fruit, and many vegetables, is less expensive and less dangerous; unfortunately it occurs far less commonly than excessive consumption of proteins.

Nitrogen compounds are indispensable in the preparation of *fertilizers*, which is one of the great industries of our country.

Like animals, plants require for food a constant supply of nitrogenous substances, which are, however, quite different from the proteins needed by animals, being much simpler in chemical composition. Thus, sodium nitrate, which contains but 5 atoms in its molecule, is an excellent and typical nitrogenous plant food. On the other hand, the proteins contain carbon, hydrogen, oxygen, nitrogen, sulphur, and sometimes other elements, in such complex chemical combination that each molecule is composed of thousands of atoms.

The difference in economic status between free and combined nitrogen is well shown by the fact that, although free nitrogen is everywhere available in unlimited quantities without cost, combined nitrogen, whether in foods or in fertilizers, must always be paid for at a high price. In fact, a country

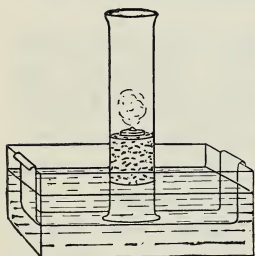


Fig. 103. Preparation of nitrogen by burning phosphorus in air.

inadequately supplied with nitrogen compounds will not be equipped for self-defense, because of the dearth of explosives, and will be in peril of famine, on account of the insufficiency of fertilizers and of foods. The great famines that take place in localities like China and India are really cases of nitrogen starvation. They occur when there is a deficiency of nitrogen compounds, though free nitrogen is everywhere present in inexhaustible abundance.

213. Preparation of nitrogen from air. Nitrogen was first obtained from air by *Daniel Rutherford*, a Scotch physician, in 1772. We have seen (§ 12) that when air is slowly passed over red-hot copper, the oxygen is absorbed by the copper, while impure nitrogen passes on and can be collected over water.

Phosphorus rapidly removes the oxygen from air, leaving impure nitrogen. A large flat cork is covered with asbestos paper and floated on water. A small piece of phosphorus is

placed on this arrangement and ignited by touching it with a hot wire, whereupon the whole is immediately covered with a jar (Fig. 103). At first the jar is filled with a white smoke of phosphorus pentoxide, P_2O_5 , but this soon dissolves in the water, and a transparent gas remains which is atmospheric nitrogen, still containing *argon* and traces of other gases.

214. Percentage of nitrogen in air. The *slow* oxidation of phosphorus in the cold affords a convenient method of analyzing air (Fig. 104). The sample of air is measured over water in a graduated tube, and a piece of phosphorus is introduced by means of a wire. If the apparatus is left over night, the oxygen will all combine with the phosphorus, and a colorless gas will remain in the tube, which is impure atmospheric nitrogen. About 1 per cent of this residual gas is *argon*, and it also contains traces of four other gases to be studied in the next chapter. The whole constitutes 79 per cent by volume of the original sample of air.

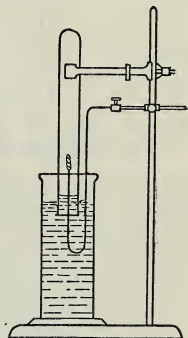
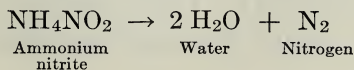


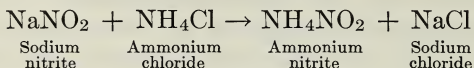
Fig. 104. Determining the percentage of nitrogen in air.

The reason for using phosphorus, rather than some other combustible element, is that its oxide is a solid and, therefore, does not mix with the nitrogen remaining. The same statement is true of copper. When *carbon*, on the other hand, is burned in air, the carbon dioxide produced is a gas, which mingles with the nitrogen and must be removed before the latter can be studied.

215. Preparation of pure nitrogen. The simplest way to obtain *pure* nitrogen is to liberate it from one of its compounds. Thus, *ammonium nitrite*, NH_4NO_2 , is a white solid which at a gentle heat decomposes according to the following equation:



Since ammonium nitrite is expensive, it is usual in the laboratory to substitute a mixture of *sodium nitrite*, NaNO_2 , and *ammonium chloride*, NH_4Cl . This mixture, when heated with a little water in the apparatus of Figure 18, yields ammonium nitrite and sodium chloride:



The ammonium nitrite then forms nitrogen and water as indicated above. The ammonium nitrite is decomposed as soon as it is formed, so that a constant current of nitrogen escapes and can be collected over water.

216. Properties of nitrogen. Nitrogen is a colorless, odorless gas, which is very slightly soluble in water. By the simultaneous application of great cold and pressure it has been converted into a colorless liquid, which freezes at a still lower temperature to an ice-like solid.

Liquid nitrogen boils at -196° and liquid oxygen at -183° . Hence, if liquid air, which is a mixture of the two, is allowed to stand, the nitrogen escapes the more rapidly, and the oxygen tends to accumulate in the residual liquid. This behavior is the basis of the method employed on a large scale for the industrial preparation of nitrogen and of oxygen.

Since nearly four-fifths of the atmosphere by volume is nitrogen, it is obvious that the gas cannot be poisonous. However, small animals placed in it are suffocated, just as they are in any atmosphere that does not provide the free oxygen without which life cannot continue.

217. Chemical conduct. Compared with oxygen, nitrogen is inactive. Striking evidence of this is the fact that many high-power incandescent electric lamps are filled with compressed nitrogen, which surrounds the glowing tungsten filament, yet does not injure it. Oxygen under the same conditions would instantly consume the incandescent filament and destroy the lamp.

In the cold, and even at a red heat, the tendency of nitrogen to combine with other elements is slight. In ordinary combustions in the air, the nitrogen merely dilutes the oxygen and retards the burning. At very high temperatures, however, nitrogen becomes more active. Thus, when a current of air is blown through an electric arc, some of the nitrogen and oxygen combine to form *nitric oxide*, NO , a fact which has found important industrial applications (§ 253). When electric sparks are passed through a mixture of nitrogen and hydrogen, or when the mixture is compressed and passed at a red heat over certain catalyzers, *ammonia*, NH_3 , is formed (§ 236). Large quantities of ammonia are manufactured by the second of the methods just referred to. *Magnesium*, when heated in nitrogen, combines with it, as does also *calcium*.

Compounds produced when nitrogen combines with other elements are called *nitrides*. Impure *magnesium nitride* is easily obtained by merely setting fire to a heap of powdered magnesium on a thick asbestos plate. On cooling, the mass is found to be covered with a white crust of *magnesium oxide*, MgO , while the interior, where the oxygen has not penetrated, consists of a yellow powder of *magnesium nitride*, Mg_3N_2 .

SUMMARY

Nitrogen prepared from air contains 1 per cent of **argon**, as well as traces of four other gases closely related to argon. Atmospheric nitrogen is easily obtained by removing the oxygen from air by means of an element of which the oxide is a solid. Either copper or phosphorus is suitable.

Nitrogen is a colorless, odorless gas, which, like all other gases, has been liquefied and solidified. Although non-poisonous, it suffocates small animals placed in it.

In the cold, and even at a red heat, nitrogen is rather **inactive**, but at very high temperatures it combines slowly with a number of other elements.

Compounds of nitrogen are of the utmost importance as

explosives and in the fertilizer industry. A class of complex nitrogen compounds, which also contain carbon, hydrogen, oxygen, sulphur, and other elements, is called the **proteins**. The proteins are indispensable in the diet.

EXERCISES

1. What is the reason for selecting copper or phosphorus, rather than some other combustible element, in obtaining nitrogen from air?
2. What is the principle of the method used on a commercial scale to produce nitrogen and oxygen from air?
3. How many grams of (a) sodium nitrite, NaNO_2 , and (b) ammonium chloride, NH_4Cl , are needed, when heated together, to yield 11.2 liters of nitrogen?
4. What are *proteins*? Mention some foods rich in them.
5. Compare the nitrogen compounds essential in the diet of animals with those fitted to serve as food for plants.
6. How can ammonia be made from nitrogen and hydrogen?
7. Compare the chemical conduct of nitrogen with that of oxygen.
8. How can the nitrogen and oxygen of the air be made to combine?

CHAPTER XXII

THE ATMOSPHERE; LIQUEFACTION OF GASES

218. Composition of the atmosphere. Neglecting water vapor, which has already been discussed, air is made up approximately as follows:

	Percentage by Volume
Nitrogen.....	78.00
Oxygen.....	21.00
Carbon dioxide.....	0.04
Argon.....	0.96
Neon	}
Helium	
Krypton	
Xenon	
	traces
	100.00

The nitrogen, oxygen, carbon dioxide, and water vapor of the air are essential to the life of animals and plants, but argon and the four gases that follow it in the table above seem to have no influence on animal and vegetable organisms.

Imagine the constituents of the atmosphere, including the water, to be separated at standard temperature and pressure and arranged in layers in the order of specific gravity, the heaviest at the bottom. All the substances would be gaseous except the water. The result would be as follows:

Substance	Depth of Layer
1. Liquid water.....	5 in.
2. Carbon dioxide.....	10 ft.
3. Argon.....	240 ft.
4. Oxygen.....	1 mile
5. Nitrogen.....	4 miles

219. Air is a mixture, not a compound. Thousands of accurate determinations of the percentage of oxygen by volume in air have been made over land and water, at different levels, in widely separated localities, and under diversified weather conditions. The results always fall between 20.9 per cent and 21 per cent by volume. This variation is so small that the question arises whether the nitrogen and oxygen of the air are chemically combined or merely mixed. The following facts

make it certain that the air is a mixture, not a compound.

1. *The variation in composition*, though slight, is sufficient to prove that the air is a mixture. *A chemical compound shows no variation whatever in the proportions of its constituents.*

2. *The behavior of liquid air* (§ 227), from which the nitrogen evaporates first and the oxygen later, shows that it is a mixture. A compound would evaporate unchanged, so that the composition of the gas that had escaped would be the same as that of the liquid that was left.

3. *The chief properties of air are merely those of the two gases that are its main*

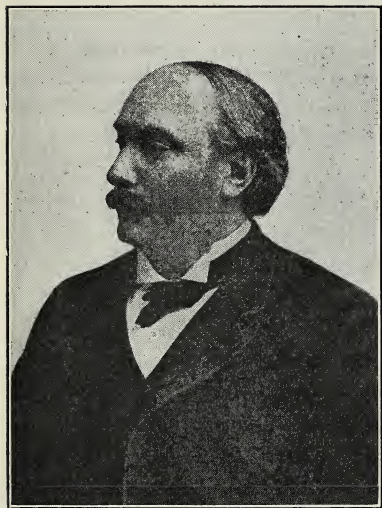


FIG. 105. JOHN WILLIAM STRUTT, BARON RAYLEIGH (1842-1919.)

English physicist, professor of natural philosophy in the Royal Institution; discovered (with Ramsay) argon and made notable contributions to the theory of sound and other branches of physical science.

constituents. When nitrogen and oxygen are mixed in the proper proportions, the product closely resembles air; no abrupt change in properties accompanies the mixing, nor is

any heat evolved. On the other hand, the *compounds* of nitrogen and oxygen, which will be studied in Chapter XXIV, are suffocating or poisonous gases, showing no resemblance to air and quite incapable of supporting the life of animals.

4. When air is *forced through a porous plate* of plaster or unglazed porcelain, the nitrogen penetrates the plate more rapidly than does the oxygen, for the gas that filters through is richer in nitrogen than is the original air. Rubber, on the other hand, allows oxygen to escape much more rapidly than it does nitrogen, so that the gas in an automobile tire that has not been pumped up for a long time is chiefly nitrogen. This is evidently the conduct of a mixture, not of a compound.

5. *Rain water contains air* which has been dissolved from the atmosphere. By boiling the water this air can be driven out and collected. When analyzed it is found to contain 34 *per cent by volume of oxygen*, instead of 21 per cent, the proportion in the atmosphere. Since this difference provides a more liberal supply of oxygen for aquatic life, it is an important matter from a biological standpoint. This difference in composition between dissolved air and ordinary air proves that air is a mixture, for gases that are chemical compounds dissolved in water unchanged and when expelled by heat still retain their original compositions.

THE INERT GASES OF THE ATMOSPHERE

220. Argon. Argon was discovered by *Lord Rayleigh* and *Sir William Ramsay*, two English scientists, in 1895. It was first obtained by passing purified air through a tube filled with red-hot copper filings. The copper absorbs the oxygen. The nitrogen is then removed in a similar way, using, instead of copper, magnesium filings heated to low redness. The residual gas which passes over both glowing metals without being affected is **argon**. It constitutes nearly 1 per cent of the original sample of air. Argon is now made from the commercial

oxygen prepared from liquid air, which is much richer in argon than is the atmosphere in general.

The *symbol* of argon is A, and since the molecule contains but 1 atom, the *formula* is A also. Its atomic weight is about 40, and it is, therefore, about 20 times as dense as hydrogen.

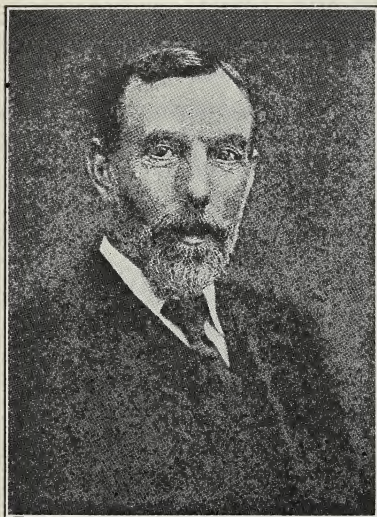


FIG. 106. SIR WILLIAM RAMSAY
(1852-1919.)

Scotch chemist, professor of chemistry in University College, London; discovered argon (with Rayleigh) and the other rare gases of the atmosphere; identified helium as a disintegration product of radium.

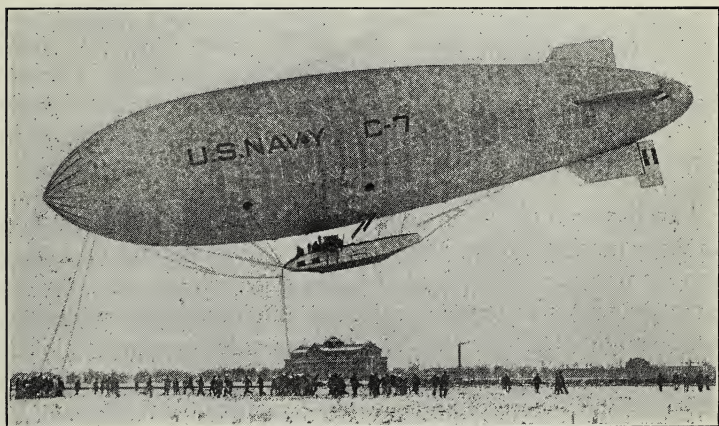
Argon is a colorless gas. It is more easily liquefied and solidified than nitrogen and is more soluble in water. It is without action on the body. The name "argon" is from the Greek equivalent of "lazy," and means *without energy* or *inert*. This refers to an extraordinary property of the gas. Careful work has led to the surprising discovery that argon is *totally inactive* chemically. Rayleigh and Ramsay were unable to induce it to enter any chemical change, and all subsequent attempts, like theirs, have failed. *Compounds of argon are unknown.*

Neon, Helium, Krypton, and Xenon. Almost all

that has been said of argon applies also to the four elements neon, helium, krypton, and xenon. Like argon they are colorless, odorless gases, the molecules of which contain but 1 atom. They are *completely inactive*, forming no compounds and taking part in no chemical changes.

Helium (He=4) is of special interest as being a product of

the disintegration of the atom of *radium* (§ 625). It is of all gases the most difficult to liquefy, and hence it is employed in filling thermometers that are to be used at very low temperatures. The formula of helium shows that its specific gravity referred to hydrogen is 2. Referred to air its specific gravity is $\frac{4}{29}$, or 0.138. Thus, helium is less than one-seventh as dense as air and, with the exception of hydrogen, is the lightest of gases. Since its lifting power is nearly as great as that of



Photograph from World Wide Photos.

Fig. 107. The U. S. Navy dirigible C-7, the first helium-filled airship.

hydrogen, helium is a very suitable gas for filling airships and captive balloons. It has the advantage over hydrogen of being non-inflammable, which insures the balloon against destruction by fire caused by bullets or shells, or by the engine. For this purpose helium can be obtained from certain kinds of natural gas occurring in the United States, which contain it in notable quantities; in fact, only the United States possesses in its natural gases sufficient helium to maintain a fleet of helium dirigibles. In order to separate the helium, the natural gas is subjected to intense cooling, whereby the methane and other

gases present are converted into liquids, while the helium remains gaseous. At the close of the World War this process was being largely developed for military purposes in the United States.

221. Proportion of the inactive gases in air. One cubic meter of air, which is 1,000,000 c.c., contains the following quantities of these inactive gases, stated in cubic centimeters:

	Cubic Centimeters
Argon.....	9,600
Neon.....	12
Helium.....	4
Krypton.....	0.05
Xenon.....	0.006

In order to get some idea of these quantities, imagine that it were possible to see the molecules of the air and that they moved past the observer at the rate of 1 each second. On the average, about 12 oxygen molecules and 48 nitrogen molecules would go by each minute. The others would be only occasional. An argon molecule would appear in the procession every 100 seconds, and a neon molecule every 3 months. A helium molecule would pass once in 10 months, and a krypton molecule once in 63 years, but it would be necessary to wait for 520 years to see a xenon molecule move by. There is, in fact, a much higher percentage of gold in an average sample of sea water than of xenon in the air.

RELATION OF THE CONSTITUENTS OF THE AIR TO LIFE

222. 1. Oxygen. Oxygen is essential, not only to all animals, but to almost all plants. That oxidation is the chemical basis of animal life becomes evident when we compare the composition by volume of the air that leaves the lungs with that of the air that enters them:

COMPOSITION OF PURE AND EXPIRED AIR

	Oxygen, per cent	Nitrogen, per cent	Argon, per cent	Carbon Dioxide, per cent
Pure air.....	21	78	0.96	0.04
Expired air.....	16	78	0.96	5.04

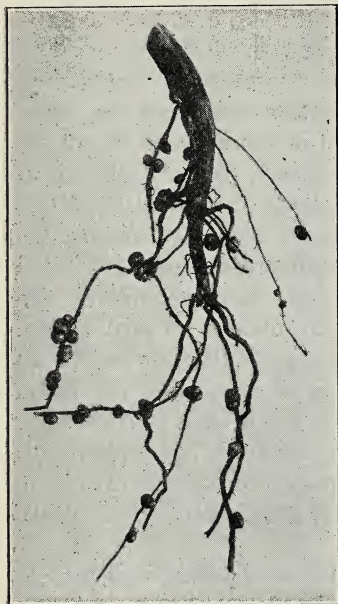
2. **Water vapor.** If the atmosphere contained no water vapor, there would be no rain, and in the absence of rain no plant life could exist. Thus, the water vapor of the air is essential to plants and through plants to animals also. A desert is simply a locality in which, for some local reason, the amount of water vapor in the air is abnormally small.

3. **Nitrogen.** We have seen how nitrogen dilutes the oxygen of the air and moderates the intensity of combustion. If the atmosphere consisted of oxygen alone, it would be impossible to use stoves and grates of iron, since the metal would burn as readily as the fuel. It would seem that a similar protective action of the nitrogen occurs in respiration, for animals do not remain in health if made to breathe pure oxygen. A condition resembling pneumonia gradually sets in, and death soon results.

Nitrogen is essential to the *nutrition of plants*, which build up, from the simple nitrogen compounds supplied by the rain and the soil, a class of highly complex nitrogen compounds called *proteins*, which serve as food for animals. Most plants, however, are unable to utilize *free* nitrogen. Wild plants depend upon traces of nitric acid, HNO_3 , and ammonia, NH_3 , which are formed in the atmosphere under the influence of electric discharges and are carried down into the soil by rain. Cultivated plants are *fertilized* with nitrogen compounds.

The botanical order of *leguminous plants*, which includes peas, beans, clover, etc., forms an important group of crops which require no nitrogenous fertilizers, for, unlike other plants,

they are able to nourish themselves from the free nitrogen of the air. Upon the roots of such plants are found nodules (Fig. 108) which contain innumerable bacteria of a peculiar species (*bacterium radicola*). These bacteria oxidize the free



Courtesy of the Bureau of Plant Industry.

Fig. 108. Nodules of nitrogen-fixing bacteria on cowpea roots.

nitrogen of the air to nitrates, like potassium nitrate, KNO_3 . Some of the nitrate remains in the soil, while some is passed on to the plant, which employs it as a basis for the manufacture of protein. An important practical result of this is that a *leguminous plant enriches the soil in nitrogen compounds for following crops*. It is often cheaper to grow a leguminous crop than to purchase nitrogenous fertilizers.

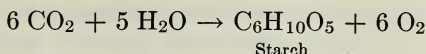
When organic matter rots in the soil, its nitrogen chiefly takes the form of *ammonia*, which is rapidly oxidized to nitrates. This is the reason for the value of decaying animal matter as a fertilizer.

Thus nitrogen, like oxygen, passes through a cycle in nature.

The animal uses the plant as food and assimilates its proteins. The nitrogenous matter of the animal passes in the soil into ammonia and then into nitrates, which are, in turn, assimilated by the plant and converted into proteins (Figure 109).

4. Carbon dioxide. The carbon dioxide of the air, though it amounts to only 4 parts by volume in 10,000, is important, for it is necessary to the life of plants. Under the influence of sunlight the leaves of plants decompose the carbon dioxide and

return the oxygen to the air. The carbon combines with water, which is always present in the leaves, to form starch, which has the formula $C_6H_{10}O_5$:



In this chemical change *energy is absorbed from the sun's rays and stored up in the starch*. This explains the fact that plants are unable *in the dark* to liberate oxygen from the carbon dioxide of the air. The formation of the starch requires a constant supply of energy from the sun, and it cannot continue when the solar rays are withdrawn.

This synthesis of starch in the leaves of plants from carbon dioxide and water may well be called the most important of all chemical changes, for it is here that is garnered the energy which is afterwards drawn upon to run all the vital processes, not only of the plants, but of the animals that are dependent upon them for food. The energy stored up when the starch is formed is liberated again as needed by the gradual oxidation of the starch and of other substances which are formed from it in the bodies of plants and animals. It follows that the energy that appears as heat and motion in the animal body is really transformed sunshine.

Unfortunately the plants utilize only about one one-thousandth of the energy of those solar rays which reach the earth. During 2 hours of summer sunlight the sun pours upon the surface of the United States a thousand times as much energy as could be obtained by burning the whole annual coal output of the world, but all but the merest trace of this energy is dissipated unused into space. An efficient means of storing and

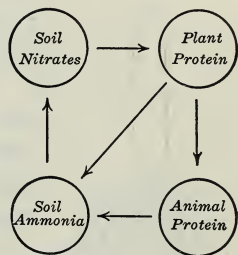


Fig. 109. Nitrogen cycle in nature.

utilizing the energy of the sun is one of the great needs of the human race.

The action of plant leaves upon carbon dioxide in sunlight is illustrated in the experiment shown in Figure 110. The flask is packed with fresh sprigs of mint and is filled with a solution of carbon dioxide in water. The inverted test tube contains the same liquid. So long as the apparatus is in the dark, there is no result, but when it is placed in sunlight, bubbles of a colorless gas collect in the test tube, which the spark test shows to be *oxygen*.

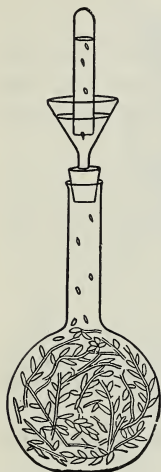


Fig. 110. Action of plant leaves on carbon dioxide.

The total quantity of carbon dioxide in the atmosphere is 2,200 billion tons. To produce this, 600 billion tons of charcoal would have to be burned, an amount which would cover the whole earth with a layer of charcoal 1 mm. ($\frac{1}{25}$ in.) thick. Forty-five billion tons of carbon dioxide, which is about one-fiftieth of the total, is withdrawn annually from the air by plants. An acre of forest absorbs about a ton of carbon dioxide per day. Plants grow more rapidly and bloom more luxuriantly in air artificially enriched with carbon dioxide, but a very large excess (8 per cent) injures the plants.

Animals continually remove oxygen from the air and discharge carbon dioxide into it. By the respiration of the human race alone about 440 million tons of carbon dioxide is annually added to the atmosphere, and the amount produced by the burning of coal is 8 times as great. In spite of all this, the percentages of oxygen and of carbon dioxide in the air have not changed since exact analyses were first made. From this it follows that each year the plants remove from the atmosphere just about as much carbon dioxide as the animals discharge into it, so that the two effects balance, and the percentages of

oxygen and of carbon dioxide remain the same. Thus carbon passes through a *cycle* in nature (Fig. 111).

The carbon dioxide of the air is absorbed by plants, which reject the oxygen and build the carbon into their structure. During the decay of the plant the carbon is slowly reoxidized to carbon dioxide and returned to the atmosphere. Should the plant be eaten by an animal, the carbon forms part of the animal's structure for a time, but is finally oxidized to carbon dioxide and returned through the lungs to the air from which it came.

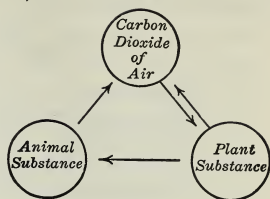
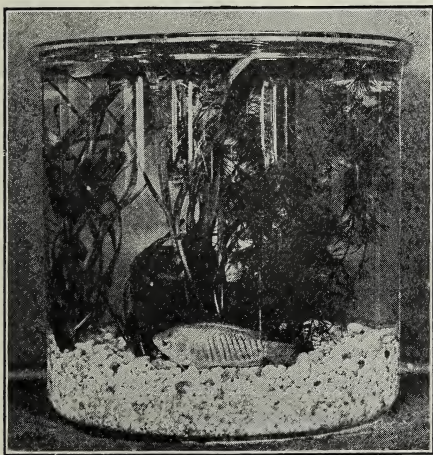


Fig. 111. Carbon dioxide cycle in nature.



Courtesy of the New York Zoölogical Society.

Fig. 112. In the balanced aquarium the carbon-dioxide cycle is complete, the fish supplying carbon dioxide to the plants, which in turn restore oxygen to the water.

223. Ventilation. An

average man produces 500 liters of carbon dioxide per day, while about 10,000 liters of air pass through the lungs. An ordinary gas burner produces about as much carbon dioxide as 5 persons, and an oil lamp discharges more carbon dioxide for the light obtained than does gas.

From this it will be seen that unless provision is made for constant renewal, the air of an ordinary room will soon differ seriously

in composition from normal air. That this is in fact the case is shown in the table below, in which are given the

percentages of carbon dioxide actually detected in a number of samples of indoor air:

Interior	Percentage of Carbon Dioxide
Schoolroom.....	0.24
Sitting room in dwelling.....	0.30
Public library.....	0.20
Bedroom, windows closed.....	0.23
Average in mines.....	0.78
Sleeping cabin in canal boat.....	0.95

In all the above instances the percentages of carbon dioxide are much higher than they should be, for although small quantities of carbon dioxide are not in themselves unwholesome, they indicate that the air is impure. The percentage of carbon dioxide in the air of any interior ought never to exceed 0.1 per cent, and ventilation is not good unless the carbon dioxide is kept below 0.07 per cent. This degree of purity can be maintained by supplying 3,000 cu. ft. of fresh air per person each hour. For ventilation a window should be open at both top and bottom.

The fact that *lime water* becomes milky on contact with carbon dioxide serves as the basis of a convenient test by which the ventilation of a room can be controlled. Select a bottle holding 300 c.c., leave it open for a time in the room to be tested, and place in it 15 c.c. of clear, saturated lime water. Cork the bottle and shake vigorously. If the liquid remains perfectly clear, the ventilation is satisfactory. Any loss of transparency indicates the need of increased air supply.

224. The dust of the air. The presence of *dust* in the air is evident when a beam of light is admitted into a dark room. The visibility of the beam is due entirely to countless solid particles, which, though heavier than air, are kept suspended by the winds. Air that would commonly be regarded as clear may contain as many as a million dust particles in each cubic foot.

The dust of the air consists of a great variety of substances. Much of it is mineral matter, picked up by the winds from dry surfaces of roads and fields. Occasionally volcanic eruptions discharge enormous quantities of dust into the atmosphere, and under favorable conditions this dust may be carried for thousands of miles. Sea air contains crystals of sodium chloride, which may be blown far inland. In all parts of the British Isles the air constantly contains salt, and in our own country it has been detected in the air of Ohio, 500 miles from the Atlantic seaboard.

The microorganisms of the air are found clinging to particles of dust, but fortunately they are far less numerous than the latter, averaging about 150 per cubic foot. They consist largely of yeasts, moulds, and putrefactive bacteria. These are useful because they attack dead animal and vegetable matter, converting its nitrogen into ammonia, which serves for the nutrition of plants. This activity of the putrefactive bacteria is the cause of the strong odor of ammonia that is often noticeable in a stable or near a manure pile. Among the bacteria of the air, however, are present the germs of air-borne diseases, like influenza, pneumonia, and ordinary colds.

Twilight is due to the downward reflection of the last rays of the sun, after it has sunk below the horizon, by the suspended matter of the air. The dust particles also assist the formation of mist and rain by offering nuclei around which the water can collect to form drops. If the air were dust-free, it is likely that rain would be infrequent and that it would be violent and destructive when it did occur.

LIQUID AIR AND THE LIQUEFACTION OF GASES

225. The nature of liquefaction. In a liquid the molecules are crowded more closely than in a gas. The same number of molecules that in a gas occupy the volume of a liter are in a liquid packed into a space of a cubic centimeter or thereabouts.

One might imagine that under these conditions the molecules of a gas would settle and form a thin layer of liquid in the bottom of the vessel, but this settling is prevented by the fact that the molecules are moving in straight lines at a speed of about half a mile per second. This incessant motion keeps them evenly distributed in the space open to them, no matter how large.

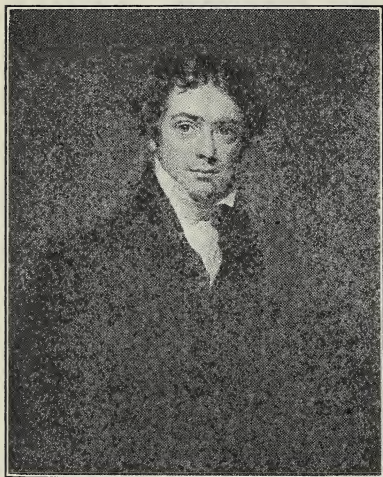


FIG. 113. MICHAEL FARADAY
(1791-1867.)

English physicist, assistant and successor to Davy as professor of chemistry in the Royal Institution; discovered benzol, liquefied several gases, and contributed much to electrochemical and electromagnetic theory.

The molecular theory, therefore, suggests three possible methods of liquefying gases:

1. *To compress the gas, thus forcing the molecules into a smaller space.* When this plan is investigated by experiment, it is found that some gases, for example, ammonia and sulphur dioxide, can easily be liquefied by pressure, but that others, like oxygen, nitrogen, and hydrogen, show no evidence of liquefaction when compressed at ordinary temperatures. Pressures of thousands of atmospheres, for instance, have been applied to oxygen, but the only result

was an enormous shrinkage in volume, no liquid being obtained. There is for each gas a temperature, called the **critical temperature**, above which no pressure, however great, will liquefy it. If the critical temperature of a gas is above the ordinary temperature of the air, liquefaction occurs when the gas is compressed, but a gas like oxygen, of which the critical

temperature is $-119^{\circ}\text{C}.$, will remain a gas above that temperature no matter what pressure is applied to it.

2. *To cool the gas, thus robbing the molecules of the motion which keeps them apart.* The test of this possibility by experiment shows that all gases can indeed be liquefied by simple cooling. The defect of the plan is that the temperature required in many cases is so low that it is difficult to reach it. Thus hydrogen, under atmospheric pressure, requires a temperature of $-253^{\circ}\text{C}.$, and helium only assumes the liquid state at $-268.5^{\circ}\text{C}.$, which is within 4.5° of the absence of all heat.

3. *To combine methods 1 and 2 above, applying pressure and cold simultaneously.* This method, after much brilliant work, has led to the liquefaction of all gases. Helium was the last to yield.

226. The Faraday tube. The English physicist, *Michael Faraday*, was the first to attack the problem of liquefaction in a systematic way. He employed a tube of thick glass (Fig. 114) bent at a right angle. In one limb was placed a solid which, when warmed, would generate the gas that he desired to liquefy, after which the tube was sealed. The end containing the solid was then heated, while the empty limb was cooled in ice or in a mixture of ice and salt.

In this simple device the pressure is furnished by the continuous production of the gas in a space from which it cannot escape, and the cooling by the ice that surrounds the empty limb. The experiment should be carried out behind a glass screen, since the pressure may burst the tube, which would involve grave danger to the eyes. Faraday had no difficulty in liquefying chlorine, carbon dioxide, ammonia, and many

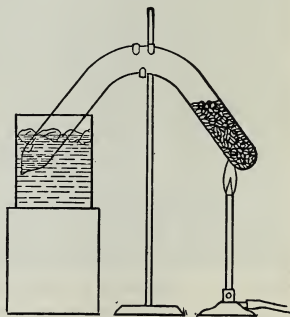


Fig. 114. Faraday's apparatus for liquefying gases.

other gases in this way. Others, like hydrogen, nitrogen, and oxygen, showed no evidence of liquefaction.

Subsequent workers have used powerful pumps to compress the gases and have employed more efficient means of cooling. By means of liquid air temperatures below -200°C . are easily

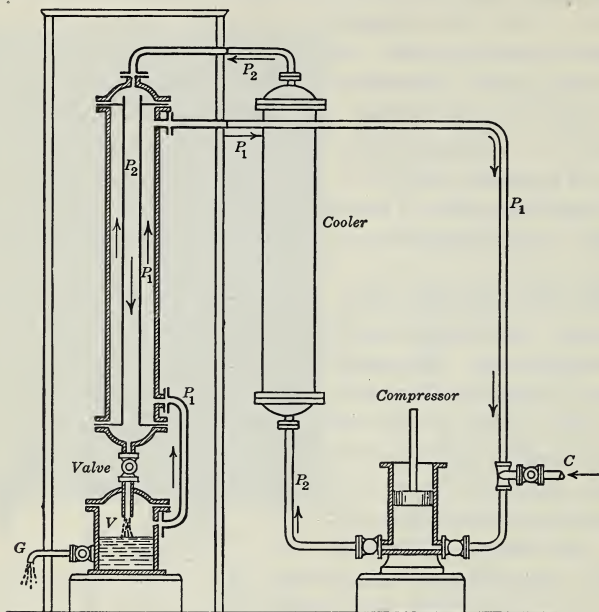


Fig. 115. Apparatus for the liquefaction of gases by self-intensive cooling.

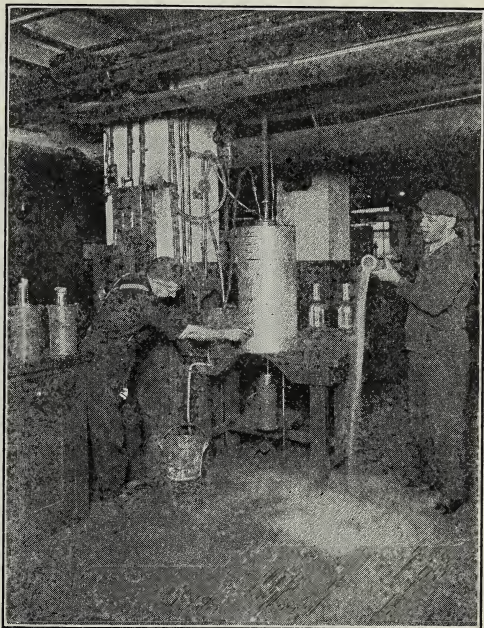
obtained; helium, boiling rapidly in a vacuum, yields the lowest temperature yet reached, -272°C ., which is within 1° of the absolute zero.

227. Self-intensive cooling. The only process that is cheap enough to liquefy air and similar gases on a commercial scale is *self-intensive cooling*. This is based on the fact that when a compressed gas is allowed to expand, it becomes cooler, because there is a slight attraction between the molecules

of gases, and energy is used up in separating them. By an ingenious device the cooling can be accumulated until the gas is so cold that it is liquefied.

A diagram of the apparatus is shown in Figure 115. The air is admitted at the intake C , which is then closed. The next step is to compress the air to 200 atmospheres in a cooler which is surrounded by water to carry off the heat produced. The air then makes its way through P_2 into the liquefying apparatus, which consists simply of a double copper tube. The compressed air passes downward through the inner tube into the vessel V , where it expands and is slightly cooled (say $1^\circ \text{C}.$). Taking the temperature of the room

as $20^\circ \text{C}.$ ($68^\circ \text{F}.$), that of the expanded gas is $19^\circ \text{C}.$ From V it follows the upward-pointing arrows through P_1 to the space between the outer and inner tubes. Thus the freshly compressed air in P_2 on its way to V is cooled by the colder expanded air which surrounds it. This second quantity of air will have a temperature of $19^\circ \text{C}.$ *before it expands*, and will



Photograph from Ewing Galloway.

Fig. 116. Liquid air is extremely volatile but can be handled and stored in vacuum-insulated containers.

drop to 18°C . afterward. Thus the temperature in the liquefier falls until, after an hour or so, liquid air can be run off at *G*, while fresh air is introduced at *C* when necessary. In the actual apparatus the double copper tube P_1 , P_2 has a total length of 100 m. It is not straight, as in the diagram, but is wound into a spiral to give compactness to the machine.

228. Properties of liquid air. Liquid air is blue. When poured upon the floor it instantly evaporates. Its temperature is -192°C ., and it produces a cloud of condensed water drops

in air, just as ice does. A kettle containing liquid air boils violently when placed upon ice. Over a flame the liquid boils still more energetically, and the bottom of the kettle becomes covered with a snowy layer, which consists of the combustion products of the gas flame—water and carbon dioxide—solidified by the extreme cold.

A rubber ball that has been cooled in liquid air breaks like an eggshell when dropped on the floor, and a tin cup that has been immersed in the liquid flies to

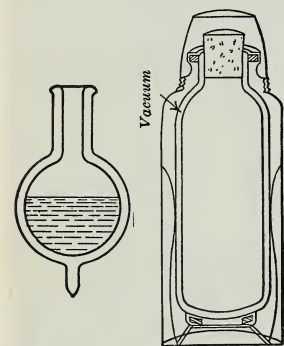


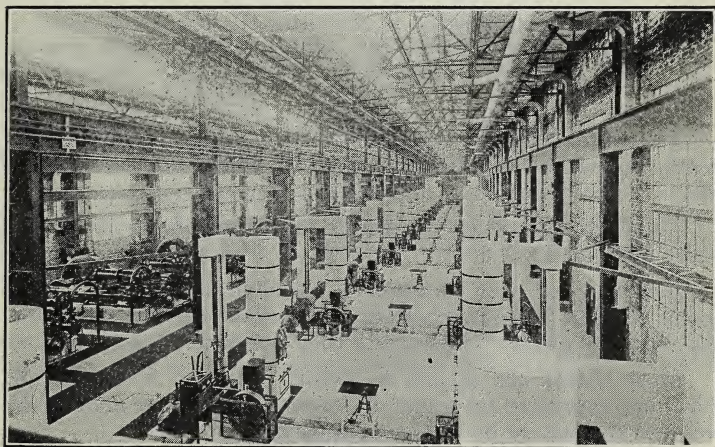
Fig. 117. The Dewar flask and its household modification, the "Thermos" bottle.

pieces when struck with a hammer.

No attempt is made to keep liquid air in sealed vessels, for the pressure that would be developed, over 22,000 lb. to the square inch, would burst any container. Moreover, even though the vessel withstood the pressure, the liquid would pass into gas when the critical temperature was reached. The only way to preserve liquid air is to prevent *heat* from finding access to it, for, like all liquids, it must absorb heat in order to evaporate. The best possible non-conductor of heat is a *vacuum*, and liquid air can be kept for hours, or even for days, in a vessel with double walls between which a vacuum has been made

(Fig. 117). Such vessels, which are known as Dewar flasks, are made of many different shapes for special purposes. Often the inside surface of the glass is silvered, which adds greatly to the efficiency. The "Thermos" bottle is simply a vacuum-jacketed container of this type, provided with a metal case and a stopper.

If the whole atmosphere could be passed through a machine like that shown in Figure 115, the liquid obtained would cover the earth to a depth of 10 m. This ocean of liquid air would



Courtesy of the Bureau of Ordnance.

Fig. 118. Liquid air compressors and fractionating columns for separation of nitrogen and oxygen at the United States Nitrates Plant at Muscle Shoals, Alabama.

not be clear blue, like the laboratory product, but would be made turbid and white by suspended crystals of ice and carbon dioxide.

229. Oxygen and nitrogen from liquid air. The chief practical application of liquid air is for the production of oxygen and nitrogen, both of which have important industrial uses. The basis of the separation is the fact that the boiling point of

liquid nitrogen (-194°) is 12° lower than that of liquid oxygen (-182°). An imperfect separation can be effected by merely allowing liquid air to trickle down through a tall tower packed with marbles. Pure liquid oxygen collects at the bottom, while gaseous nitrogen containing a little oxygen escapes at the top. The apparatus actually employed on a commercial scale resembles the *column still* used in separating alcohol from water, which will be described later (§ 590). The gas as it nears the upper end of the column is sprayed with liquid nitrogen, which at once condenses the oxygen, so that practically pure nitrogen is obtained.

SUMMARY

Air contains about one-fifth of its volume of **oxygen** and nearly four-fifths of **nitrogen**, both of which are essential to life.

These two gases are **mixed** in the atmosphere, not chemically combined.

Nearly 1 per cent of argon is found in the air, as well as traces of **neon**, **helium**, **krypton**, and **xenon**. All five are colorless, odorless gases. Chemically they are **totally inactive**.

Most plants are unable to absorb nitrogen from the air. They are nourished by traces of ammonia and nitric acid in the soil and the rain or by nitrogenous fertilizers.

Leguminous plants, like peas, beans, and clover, have upon their roots bacteria of a special kind. These convert free nitrogen into nitrates, which then nourish the plant. *The growth of a leguminous plant stores up nitrates in the soil for succeeding crops.*

Nitrogen and carbon, like oxygen, pass through a *cycle* in nature. A cycle is a series of changes that repeats itself.

The **carbon dioxide** of the air is necessary to plants. In the leaves **starch** is formed from carbon dioxide and water, oxygen being returned to the air. The *energy* that is absorbed from sunlight in this one chemical change is drawn upon later to support all the life processes of plants and animals.

The **percentages** of oxygen and of carbon dioxide in the air **remain the same**. This is because the effects of the animals and the plants upon the composition of the atmosphere are equal and opposite.

The carbon dioxide in the air of rooms should be kept below 0.07 per cent. This can be done by supplying 3.000 cu. ft. of fresh air per person per hour. For **ventilation** a window should be opened *at both the top and the bottom*.

The dust of the air consists of fine particles of mineral, animal, and vegetable origin and of microorganisms, which, however, are few in proportion to the dust particles.

Some gases can be liquefied at ordinary temperatures by pressure alone; others cannot. For each gas there is a **critical temperature**, above which no pressure, however great, will convert it into a liquid.

By the joint action of pressure and cold **all gases have been liquefied**.

Self-intensive cooling depends upon accumulating the slight cooling effect of allowing a compressed gas to expand. This is the method adopted in the liquefaction of difficult gases on a commercial scale.

The most important use of **liquid air** is for obtaining nitrogen and oxygen separately. The possibility of this depends upon the fact that the boiling points of the two elements differ by 12° C.

EXERCISES

1. What four constituents of the air are necessary to life? What is the part played by each?
2. State five facts that prove that the nitrogen and oxygen of the air are mixed, not combined.
3. How was argon first obtained? What is the peculiarity of its chemical conduct? In what ways do the other inert gases of the atmosphere resemble argon?
4. What is the effect upon the soil of growing a *leguminous crop*? Why?
5. Give the *cycle* of nitrogen in nature.

6. What is the source of the energy that runs the life processes of animals and plants?
7. Does the composition of the air remain the same from year to year? Why?
8. What percentage of carbon dioxide should be tolerated in the air of a room? How can the percentage be kept below the limiting figure?
9. What is meant by the critical temperature of a gas?
10. Describe the Faraday tube and the results obtained with it.
11. Explain the meaning of *self-intensive cooling*.
12. How are nitrogen and oxygen obtained on a large scale?
13. What is the principle of the "Thermos" bottle?
14. What are the advantages and disadvantages of the dust in the air?
15. What is the connection between thunderstorms and the nutrition of wild plants?
16. Taking an acre as a square 209 ft. on each side and the pressure of the air as 14.5 lb. per square inch, calculate in pounds the weight of the air above each acre of ground. About how much of this is nitrogen? Why, in spite of the great abundance of nitrogen, is it necessary to fertilize with nitrogen compounds?

REVIEW QUESTIONS

1. What do you understand by the term *radical*? What is the radical of sulphuric acid? Of the sulphates? Of nitric acid? Of the nitrates? What are the two radicals of ammonium hydroxide, NH_4OH ?
2. How do the uses of sodium differ from those of iron? Why?

CHAPTER XXIII

AMMONIA, NH_3 ; AMMONIUM SALTS

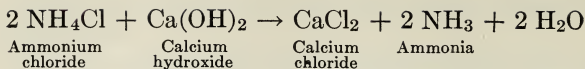
230. Occurrence. Ammonia, NH_3 , being a product of the decay of organic matter, is found in traces in the soil, in the air, in rain water, and in natural waters. The odor of ammonia is usually noticeable in a stable or near a manure pile. The presence of as much as 1 part by weight of ammonia in 10 million parts of drinking water is regarded as an indication that the water has probably been contaminated with sewage and may contain the germs of water-borne disease.

231. Formation and preparation. When a mixture of 1 part by volume of nitrogen with 3 parts of hydrogen, confined over mercury in the apparatus of Figure 62, called a *eudiometer*, is treated with electric sparks, a slow and partial combination to ammonia takes place.

Any *ammonium salt* (§ 234) when mixed with powdered lime gives off ammonia at a gentle heat. This is the basis of the laboratory preparation of ammonia.

A mixture of powdered lime with any organic matter containing *protein*, such as flour, meat, white of egg, or scraps of horn, yields ammonia when warmed. The old name of ammonia, "**spirits of hartshorn**," points to the fact that it was formerly made for medicinal use from horn.

Both nitrogen and hydrogen are contained in *bituminous coal*. When it is heated for the manufacture of coke and coal gas, ammonia is obtained as a by-product. This is an important industrial source of ammonia. In the laboratory ammonia is obtained by gently warming a mixture of *ammonium chloride*, NH_4Cl , with slaked lime, which is *calcium hydroxide*, $\text{Ca}(\text{OH})_2$; the reaction is as follows:



The apparatus is shown in Figure 119. A mixture of equal weights of ammonium chloride and calcium hydroxide is carefully heated in the flask, and the ammonia, which is much lighter than air, is collected in the inverted bottle.

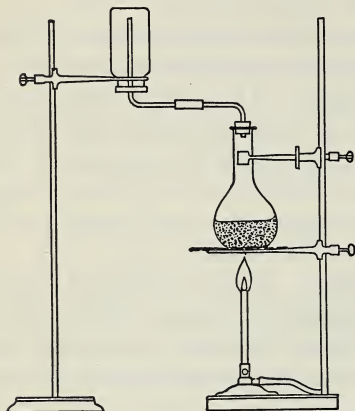


Fig. 119. Laboratory preparation of ammonia.

232. Physical properties.

Ammonia is a colorless, suffocating gas with a peculiar odor. From the formula NH_3 its molecular weight is 17. Hence its specific gravity referred to air must be $\frac{17}{29}$, or 0.59. This agrees with the result of experiment, for the gas is only a little more than half as dense as air.

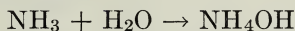
At ordinary temperatures a pressure of 7 atmospheres converts ammonia into a colorless liquid, which is sold in steel cylinders for use in ice machines. This liquid must not be confused with the **ammonia water** of the household, which is a solution of ammonia in water.

Ammonia is one of the very soluble gases. At 0° water dissolves 1,300 times its volume of ammonia, and at 20° (room temperature), 700 times. These solutions are *lighter* than water itself. The strongest *ammonia water* of commerce has a specific gravity of 0.9 and contains 35 per cent of ammonia by weight. Ammonia escapes from its water solution even in the cold and is completely expelled by boiling.

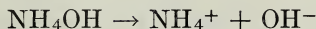
The great solubility of ammonia in water is well shown by

the "fountain experiment" (§ 117). The apparatus is the same as that shown in Figure 76, but the water in the lower vessel should in this case be colored with *red* litmus. When the water forces its way up through the jet tube into the flask, the litmus will turn *blue*, showing that ammonia water is *alkaline*.

233. Chemical conduct. The alkaline reaction of ammonia water and the fact that it neutralizes acids are due to the presence of *ammonium hydroxide*, NH_4OH , which is formed when ammonia dissolves in water:

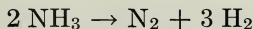


This compound, which is known only in solution, is then ionized:

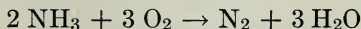


The hydroxyl ions are the cause of the marked basic properties of ammonia water.

When ammonia is led through a red-hot tube, decomposition takes place:

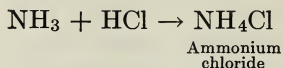


If a tube from which ammonia is escaping is held near a Bunsen flame, the ammonia burns around the flame with a peculiar yellow color, but the combustion ceases as soon as the burner ~~flame~~ is withdrawn. In oxygen, however, ammonia burns with a yellow flame which is self-supporting; the hydrogen forms water and the nitrogen is liberated:

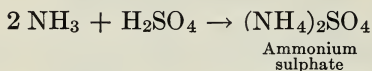
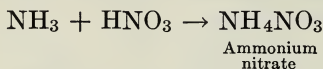


234. Combination of ammonia with acids. When a jar filled with ammonia is brought mouth to mouth with one that has been filled with hydrogen chloride, a dense white smoke of

ammonium chloride, NH_4Cl , fills both vessels and finally deposits as a white film on the glass:

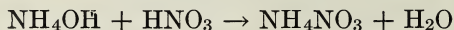
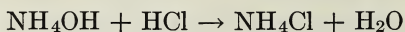


Ammonia also combines with the other acids, producing compounds in which the hydrogen of the acid is replaced by the univalent radical **ammonium**, NH_4 . For instance:



These compounds are known as the **ammonium salts**. The radical *ammonium*, NH_4 , which they all contain, must not be confused with *ammonia*, NH_3 . Ammonium is not a real substance. It is merely a group of 5 atoms which exists only in the ammonium salts and has never been obtained in the free state.

The ammonium salts can also be obtained by neutralizing aqueous solutions of acids with ammonium hydroxide; for example, ammonium chloride is formed when ammonia water is added to hydrochloric acid, and ammonium nitrate with dilute nitric acid:



Since the interaction of ammonia with active acids is violent, it is dangerous to mix concentrated ammonia water with concentrated acids. This is especially true of concentrated sulphuric acid.

INDUSTRIAL SOURCES AND USES OF AMMONIA

235. Ammonia from coal. Ammonia is formed when coal is heated for the manufacture of coke and illuminating gas. The ammonia escapes with the illuminating gas and is removed from it by washing with water (§ 283). In this way a very impure solution of ammonia known as "gas liquor" is obtained.

The "gas liquor" is sold to the manufacturing chemist, who heats it with lime, whereupon ammonia escapes as gas. The remainder of the process depends upon the product desired:

1. The ammonia can be liquefied by pressure and stored in steel cylinders for use in ice machines. This anhydrous *liquid ammonia* must be carefully distinguished from ammonia water.

2. It can be passed into a vessel containing water, in which it will dissolve to form the *ammonia water* of commerce.

3. If the ammonia is led into a solution of hydrochloric acid, *ammonium chloride*, NH_4Cl , is formed, which can be obtained in the solid state by evaporation.

4. Leading the ammonia into a solution of sulphuric acid and afterwards evaporating yields *ammonium sulphate*, $(\text{NH}_4)_2\text{SO}_4$.

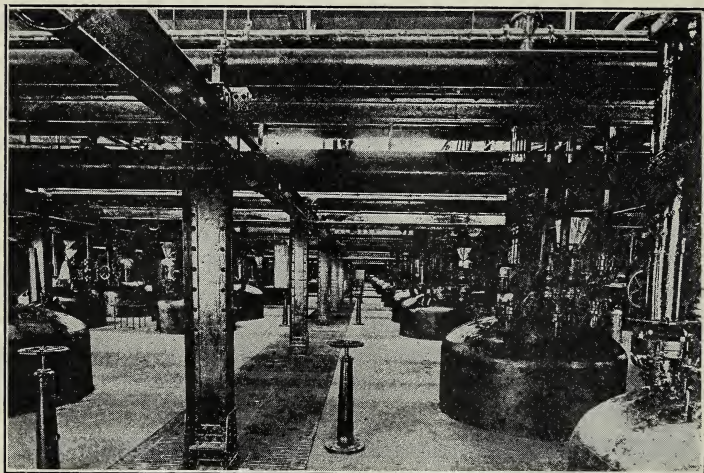
5. When dilute nitric acid is placed in the receiver into which the ammonia is passed, *ammonium nitrate*, NH_4NO_3 , is produced.

236. Commercial synthesis from nitrogen and hydrogen.

It will be remembered that nitrogen can be cheaply obtained from air and hydrogen from water. When a mixture of 3 volumes of hydrogen with 1 of nitrogen is passed, under strong pressure and at a dark-red heat, through iron tubes containing powdered iron, which acts as a catalyst, a partial combination to ammonia takes place. The gaseous mixture is then passed through a cooling coil, in which the ammonia is liquefied and from which it is removed. The uncombined nitrogen and hydrogen continue the circulation through the hot tubes containing the catalyst. During the World War large quantities of

ammonia were made in Europe by this method, which is known as the Haber process, although it was devised by the French chemist *Le Rossignol*.

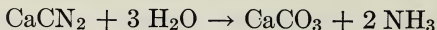
237. Manufacture of ammonia from "cyanamide," CaCN_2 . "*Cyanamide*" is the commercial name of a black substance the formula of which is CaCN_2 , which is made by heating calcium carbide, CaC_2 , in nitrogen (§ 386). It is used as a fer-



Courtesy of the Bureau of Ordnance.

Fig. 120. Autoclaves for the production of ammonia from cyanamide at the United States Nitrates Plant at Muscle Shoals, Alabama.

tilizer. When cyanamide is heated under pressure with steam, ammonia is liberated:



This important method served as the chief source of the enormous quantities of ammonia that were needed by our Government after the United States had entered the World War.

238. Uses of ammonia. One of the largest consumers of ammonia is the *Solvay process* for making sodium carbonate

(§ 168). Much ammonia is made into the three important *ammonium salts* the manufacture of which has just been sketched. They will be described presently. Ammonia is easily oxidized to *nitric acid*, HNO_3 , large quantities of which were made in this way in all the belligerent countries during the war (§ 252). A very important use of ammonia is for *refrigeration* and for the manufacture of *artificial ice*. Much of the ammonia produced is marketed in the form of *ammonia water*, which is essential in the household as a cleanser and in many industries.

239. Refrigeration with ammonia. Refrigeration by machinery is based on the fact that a liquefied gas absorbs much heat when, by reducing the pressure upon it, it is allowed to become a gas again. Liquid ammonia has displaced other substances in refrigeration because it is cheap and because when it becomes ammonia gas a large amount of heat disappears—300 calories for every gram that evaporates.

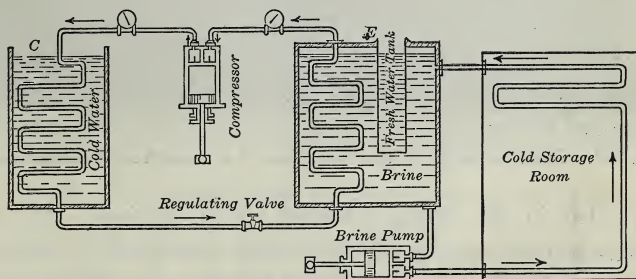
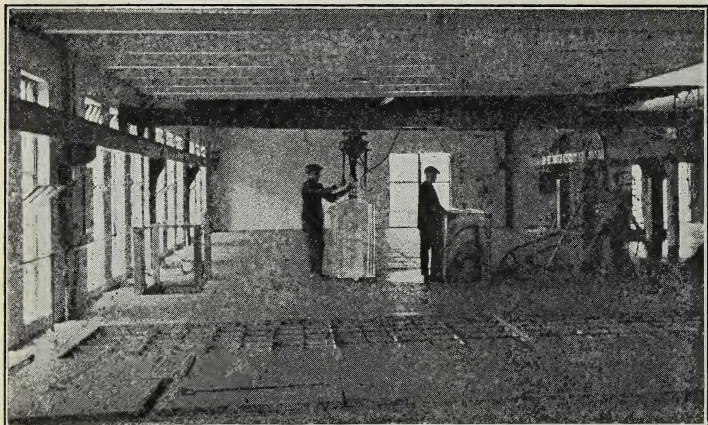


Fig. 121. Diagram of a refrigerating plant.

The diagram in Figure 121 will make clear the principle of the refrigerating machine. The ammonia is forced by a compressor operated by a steam engine into a coil of iron pipe *C*, where it condenses, liberating 300 calories of heat for every gram of ammonia that assumes the liquid state. This heat is removed by water which circulates in a tank in which the coil is immersed.

Often the coil is vertical and the cooling water trickles over it like a miniature cascade.

The liquid ammonia passes through a regulating valve into a second coil *E*, which is immersed in a tank of brine. Here, aided by the vacuum of the same compressor, the ammonia evaporates, absorbing 300 calories of heat per gram. Hence the brine becomes cold. If metal cans containing water are



Courtesy of the American Ice Co.

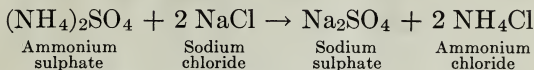
Fig. 122. Drawing blocks in the tank room of a modern artificial-ice plant.

suspended in the brine, artificial ice is obtained. In cold-storage warehouses the chilled brine is circulated by means of a pump through iron pipes supported near the ceilings of the rooms to be cooled.

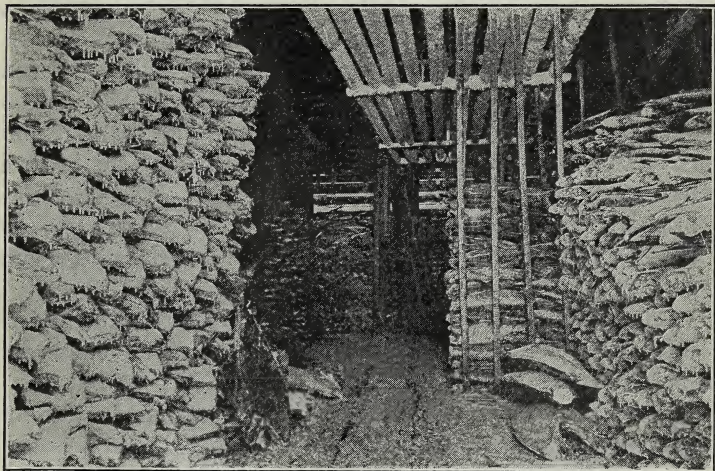
AMMONIUM SALTS

240. Ammonium chloride, NH_4Cl . The formation of ammonium chloride when ammonia and hydrogen chloride are mixed and its manufacture from "gas liquor" have been mentioned. It is also made by heating a mixture of *ammonium*

sulphate and *sodium chloride* in a pot provided with a dome-shaped iron cover:



The ammonium chloride is vaporized and condenses on the cover



Photograph from Ewing Galloway.

Fig. 123. Frozen Alaska halibut in a Seattle cold-storage warehouse.

as a solid white mass, while sodium sulphate remains in the vessel in which the mixture was heated.

Ammonium chloride is often called by its old name of “*sal-ammoniac*.” It is a white solid with a salty taste. At a gentle heat it vaporizes *without melting*, and upon cooling again becomes solid. The vapor is a mixture of equal volumes of ammonia and hydrogen chloride, for ammonium chloride is decomposed when heated:



When the vapor is allowed to cool, recombination to solid NH_4Cl occurs. Decomposition of this kind, caused by heat and reversed by cooling, is called **dissociation**.

Ammonium chloride dissolves in 3 times its weight of cold water. The solution is used in filling the so-called dry cells and other batteries that are to be used on open electric circuits. This important use consumes most of the output of ammonium chloride.

Ammonium chloride is employed to remove films of rust (oxide) from metallic surfaces before soldering. The hydrogen chloride produced when the ammonium chloride is placed upon the heated metal converts the metallic oxide in the rust film into a chloride which either vaporizes or melts and is thus removed.

Ammonium chloride is also used in calico printing, in the manufacture of dyestuffs, and in medicine, especially in cough mixtures.

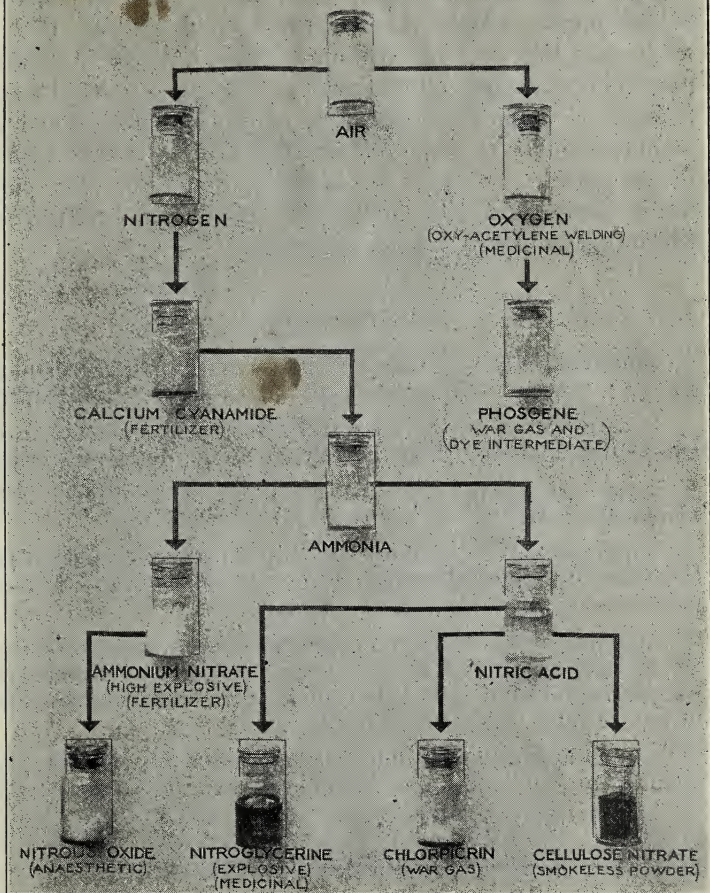
Ammonium bromide, NH_4Br , and **ammonium iodide**, NH_4I , closely resemble the chloride. They are extensively employed in photography.

241. Ammonium nitrate, NH_4NO_3 . The manufacture of this important salt has already been discussed. It is colorless, crystalline, and very soluble in water. The dissolving of ammonium nitrate is accompanied by a decided fall in temperature, so that if the beaker in which the ammonium nitrate and water are contained is stood upon a wet block of wood, the block will be frozen to the bottom of the beaker.

Ammonium nitrate is employed in making the dentist's gas, *nitrous oxide* (§ 243), but its main use is in the explosives industry. It is a constituent of many of the *safety explosives*, which are so called because when detonated they produce a small flame which lasts only for a small fraction of a second and is not likely to ignite the fire damp and coal dust which cause so many accidents in coal mines. Ammonium nitrate is also largely used in military explosives. "*Ammonal*," which

AIR PRODUCTS

IN WAR AND PEACE TIME INDUSTRIES



Courtesy of the National Research Council.

Fig. 124. Products from air and ammonia.

was so largely employed in the World War as a bursting charge for hand grenades and high-explosive shells, is a mixture of ammonium nitrate and *tri-nitro-toluene* ("T. N. T.").

242. Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$. The manufacture of ammonium sulphate has already been described. It is a white solid freely soluble in water. When heated it is decomposed and vaporized without melting. The annual production is about $1\frac{1}{4}$ million tons and is rapidly increasing. About 20 lb. of ammonium sulphate per ton of coal can be obtained when the manufacture of coke is rationally conducted. The chief use of ammonium sulphate is as a nitrogenous fertilizer, for which it is employed in large quantities.

SUMMARY

Ammonia, NH_3 , is contained in the soil, in the air, and in water. In water its presence is an indication of contamination.

It is prepared in the laboratory by heating a mixture of ammonium chloride, NH_4Cl , with calcium hydroxide, $\text{Ca}(\text{OH})_2$.

Liquid ammonia must be carefully distinguished from ammonia water.

Liquid ammonia is almost the only substance employed for large-scale mechanical refrigeration. Ammonia water is used for cleansing and for chemical purposes.

Ammonia water turns red litmus blue and neutralizes acids. These basic properties are due to the presence of **ammonium hydroxide**, NH_4OH , which is formed when ammonia dissolves in water: $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH}$.

Ammonia is obtained industrially (1) as a *by-product* in the manufacture of coke and illuminating gas from soft coal; (2) by the *direct combination* of nitrogen and hydrogen under pressure at a dull red heat in presence of a catalyst; (3) by the interaction of *cyanamide* with steam under pressure.

Ammonia, NH_3 , must not be confused with **ammonium**, NH_4 , which is a univalent *radical* known only in its compounds.

Each acid yields an ammonium salt, in which the hydrogen



of the acid is replaced by ammonium. They can be obtained either by direct combination of ammonia with acids or by neutralizing water solutions of the acids with ammonium hydroxide.

The most important ammonium salts and their chief uses are the following:

Ammonium chloride, NH_4Cl Filling dry cells
Ammonium nitrate, NH_4NO_3 Explosives
Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$ Fertilizer

EXERCISES

1. State in two parallel columns the distinctions between *ammonia* and *ammonium*.
2. How is ammonia made on a large scale from its elements?
3. Describe the manufacture of ammonia (a) from coal, (b) from cyanamide.
4. Why does ammonia water act like a solution of a base?
5. State a rule for writing the formula of the ammonium salt when that of the acid is given.
6. Give the names and formulas of the ammonium salts of the following acids; HF , H_2CO_3 , HClO_3 , H_2SO_3 , H_3PO_4 .
7. How many grams of ammonia escape when 856 grams of ammonium chloride are heated with slaked lime?
8. Calculate the percentage composition of (a) ammonium chloride, (b) ammonium nitrate, (c) ammonium sulphate, (d) ammonium hydroxide.
9. (a) How many cubic centimeters of hydrogen would be required to form ammonia with 150 c.c. of nitrogen? (b) How many cubic centimeters of ammonia would be obtained?
10. Three kilograms of 30 per cent ammonia water are to be prepared by heating ammonium chloride with slaked lime and passing the ammonia into water. How many grams of ammonium chloride must be used?
11. Calculate from the formula NH_4Cl the specific gravity of the vapor of ammonium chloride referred to air. The *actual* specific

gravity is 0.92. What conclusion do you draw from this discrepancy between theory and experiment?

12. Explain the fact that perfectly dry ammonia has no effect upon dry red litmus paper.

13. Concentrated sulphuric acid is an excellent drying agent for most gases. Could it be used for drying ammonia?

14. What is the origin of the word *ammonia* (see *Webster's Unabridged Dictionary*)?

15. Why has ammonia displaced other gases for the manufacture of ice?

16. What methods of making ammonia were used during the World War?

17. Ammonia was formerly called "*the volatile alkali*." Why?

18. How could you show that ammonium hydroxide as compared with sodium hydroxide is an *inactive* base?

19. How could you find out whether a sample submitted to you was an ammonium salt or not?

20. Why is it usual to treat acid spots upon the clothing with dilute ammonium hydroxide?

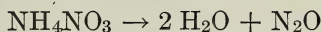
CHAPTER XXIV

OXIDES OF NITROGEN; NITRIC ACID

OXIDES OF NITROGEN

Six compounds of nitrogen and oxygen are known. They are purely laboratory products, not being found in nature. All of them differ strikingly from air. Only three, all gases, are sufficiently important to be studied here. These are *nitrous oxide*, N_2O ; *nitric oxide*, NO , and *nitrogen peroxide*, NO_2 . The others are *nitrogen trioxide*, N_2O_3 (liquid), *nitrogen tetroxide*, N_2O_4 (gas), and *nitrogen pentoxide*, N_2O_5 (solid).

243. Nitrous oxide, N_2O . Nitrous oxide, discovered by Priestley, is prepared by heating ammonium nitrate, which first melts and then decomposes:



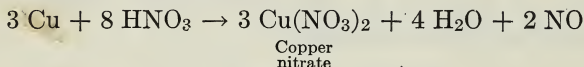
Since ammonium nitrate may explode when suddenly heated, the experiment should be performed with care. The gas dissolves in about its own volume of cold water; it is collected, therefore, over warm water to avoid loss.

Nitrous oxide is a colorless, odorless gas with a sweet taste. Sir Humphry Davy discovered that a little of it when inhaled produced intoxication (hence the name "*laughing gas*"), while more caused the subject to become insensible for a short time. This latter effect has brought about the wide use of nitrous oxide as an anæsthetic by dentists, who purchase it in liquid form in steel cylinders. It must be carefully purified before liquefaction, for the gas given off when ammonium nitrate is heated may contain nitric oxide and nitrogen peroxide, both of which are poisonous. During administration the dentist

mixes the nitrous oxide with air or with oxygen to avoid the danger of asphyxiating the patient.

Like oxygen, nitrous oxide causes a splint bearing a spark to burst into flame. It supports the combustion of a candle and of sulphur, phosphorus, charcoal, etc., far more vigorously than does air. In these experiments the *oxygen* of the nitrous oxide combines with the burning substance, and there remains a volume of *nitrogen* equal to that of the nitrous oxide consumed. Hence nitrous oxide must be decomposed before it can support combustion. For this reason sulphur that has just begun to burn is *extinguished* when lowered into nitrous oxide, whereas if the sulphur is burning with a flame that is hot enough to decompose the nitrous oxide and thus to supply itself with oxygen, the energy of the combustion is increased.

244. Nitric oxide, NO. Nitric oxide is made by the action of dilute nitric acid upon copper:



The apparatus is similar to that used in preparing hydrogen and the gas is collected over water (Figure 40).

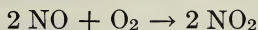
Nitric oxide is a colorless, poisonous gas. As the formula shows, its specific gravity is almost the same as that of air. It is very slightly soluble in water, and it is quite difficult to liquefy.

The oxygen of nitric oxide is firmly held; hence the gas extinguishes most burning substances. However, the combustions of phosphorus and of magnesium continue brilliantly in nitric oxide.

When air is intensely heated by blowing it through a powerful electric arc, a small percentage of nitric oxide is formed. In Norway nitric oxide is made on a large scale by this method, for immediate conversion into *nitric acid* (§ 253).

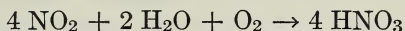
When a bottle filled with nitric oxide is opened, the gas at

once becomes warm, and its color changes to a deep reddish brown. Each molecule of nitric oxide combines with an additional atom of oxygen from the air, and *nitrogen peroxide* is formed:



245. Nitrogen peroxide, NO_2 . Nitrogen peroxide is the reddish-brown gas the evolution of which is often noticed when metals are dissolved in nitric acid. Its odor is similar to that of nitric acid and is not especially noticeable or irritating. When inhaled in any quantity, however, nitrogen peroxide is highly poisonous, and there is no antidote to its effects, since it attacks and disintegrates the delicate tissues of the lungs. Care should be taken, therefore, to avoid inhaling the gas that escapes when *nitric acid* acts upon metals or other substances.

Nitrogen peroxide in the presence of water and air dissolves to form a solution of *nitric acid*:



This behavior is applied in the Norwegian process already mentioned for the production of nitric acid from air.

Nitrogen peroxide supports combustion brilliantly, for its oxygen is abundant and loosely held. Flour exposed to air containing traces of nitrogen peroxide is bleached, and the gas has been much used for this questionable purpose. Nitrogen peroxide is extensively used as a catalyst in the manufacture of sulphuric acid by the lead-chamber process (§ 321).

NITRIC ACID, HNO_3

246. Preparation. Nitric acid occurs in traces in the air, and it is especially perceptible in the rain that falls at the beginning of a thunder-shower. The connection of this nitric acid with plant growth has already been discussed (§ 322).

Sodium nitrate, NaNO_3 , is the most abundant salt of nitric acid and is the source of much of the nitric acid of commerce.

Potassium nitrate, KNO_3 , also plays an important part in industry, though on a smaller scale than the sodium salt.

Nitric acid can be made in the laboratory by distilling sodium nitrate with an equal weight of concentrated sulphuric acid in the apparatus of Figure 125.

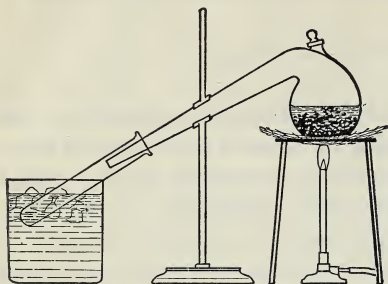
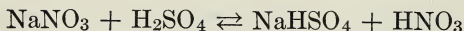


Fig. 125. Laboratory preparation of nitric acid.



Sodium
hydrogen
sulphate

The nitric acid condenses in the cooled receiver, while *sodium hydrogen sulphate*, NaHSO_4 , which is known in industry as **niter cake**, remains in the retort.

247. Chemical equilibrium. As the arrows indicate, the equation just given is *reversible*. Not only will sulphuric acid produce nitric acid from sodium nitrate, but *nitric acid will liberate sulphuric acid from sodium hydrogen sulphate*. Hence, when sulphuric acid is added to sodium nitrate in the cold, a little nitric acid is produced, but only a little, for this nitric acid at once begins to attack the sodium hydrogen sulphate that has also been formed and to liberate sulphuric acid again, so that the process comes to a standstill when the backward process balances the forward one. Such a state of things is called a **chemical equilibrium**. When this stage has been reached, if heat is applied, the nitric acid, because of its low boiling point (86°), is driven over into the receiver, where it

can exert no action on the sodium hydrogen sulphate. On the other hand, the sulphuric acid, of which the boiling point is high (338°), is able to remain in the retort and to liberate a further quantity of nitric acid which in its turn passes over into the receiver. In this manner the chemical change proceeds until the sodium nitrate is all consumed. Thus, although nitric acid is *more active* than sulphuric, the latter wins the conflict simply because it can stay in the retort, while the nitric acid is driven into the receiver as soon as it is formed.

It is plain that an attempt to prepare sulphuric acid by distilling sodium hydrogen sulphate with nitric acid would be foredoomed to failure. Some sulphuric acid would be produced when the two materials were mixed in the retort in the cold, but on heating, nitric acid would vaporize and sodium hydrogen sulphate would remain in the retort, no sulphuric acid being obtained.

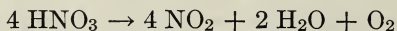
The wide use of sulphuric acid in manufacturing chemistry for obtaining other acids from their salts is based mainly on the facts that sulphuric acid is *cheap* and that it has a *high boiling point*.

Any nitrate when distilled with sulphuric acid will yield nitric acid. Sodium nitrate is used exclusively in practice merely because it is the *cheapest* nitrate.

248. Physical properties. Pure nitric acid is a colorless, fuming liquid of specific gravity 1.5, which freezes at -50° and boils at 86° . Like other active acids, it acts as an irritant poison when swallowed. Even the vapor of nitric acid is poisonous, so that when a large bottle of it is broken, the cleaning-up of the debris is a dangerous operation. The concentrated nitric acid of the laboratory contains about two-thirds of its weight of HNO_3 , the balance being water which reduces the specific gravity to 1.4.

249. Chemical conduct. The student has probably noticed in the laboratory that in the bottles that stand near the windows,

in strong light, the nitric acid is yellow or red. The explanation is that a little of the acid is decomposed by light:



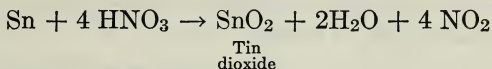
and the nitrogen peroxide formed dissolves in the remaining acid and colors it. The same decomposition occurs to some extent when nitric acid is heated and gives some trouble in its manufacture.

The formula HNO_3 shows that nitric acid contains $\frac{48}{63}$, which is almost exactly three-fourths, of its weight of oxygen. In a liter of pure nitric acid there are nearly 800 liters of oxygen, which is only loosely held. It is not surprising, therefore, that nitric acid is a violent oxidizing agent. A flame of illuminating gas goes on burning when placed beneath the surface of pure nitric acid, and finely pulverized charcoal ignites when moistened with it. The warm vapor of the acid responds to the spark test. An important practical point is that nitric acid may set fire to the hay, straw, sawdust, or shavings often used for packing bottles. It must be prepared for transportation with special care.

Proteins, like white of egg, are colored *yellow* when moistened with nitric acid. The proteins of the skin are affected in the same way. The nature of the yellow substance is not definitely known. Ammonia turns it *orange*.

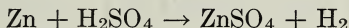
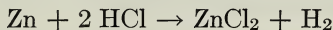
The reddish stains produced upon the clothing by hydrochloric acid or by dilute sulphuric acid can be removed by neutralizing the acid with dilute ammonia water, but the yellow spots arising from the action of nitric acid do not yield to this treatment. This is because *wool* is a protein and behaves with nitric acid like other proteins. Nevertheless, it is advisable to use ammonia with nitric-acid stains also, as it may prevent the development of a hole in the garment. The spot can afterward be colored so as to match as closely as possible the surrounding cloth.

250. Action of nitric acid on metals. The noble metals *gold* and *platinum* are unaffected by nitric acid. Its action upon *aluminum* is slight, and apparatus made of this metal is successfully used in the manufacture of nitric acid. *Tin* is rapidly converted by nitric acid to a white powder of *tin dioxide*:



Most of the other familiar metals, for instance, iron, zinc, copper, lead, silver, and mercury, dissolve rapidly in nitric acid to form *nitrates*. The last four are hardly affected by hydrochloric or dilute sulphuric acid. Thus, nitric acid is one of the most active acids known. This fact finds expression in the name **aqua fortis**, which was given to nitric acid during the Middle Ages and is still occasionally used.

It will be recalled that hydrogen is obtained when hydrochloric or sulphuric acid acts upon zinc:

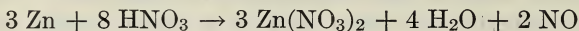


The essential thing about the interaction of an acid with a metal is that *hydrogen* escapes, and the metal takes its place in the acid molecule, forming a *salt*. In the case of nitric acid, however, the hydrogen formed does *not* escape. It is oxidized to water by another molecule of nitric acid. Thus the nitric acid acts at the same time as an *acid* and as an *oxidizing agent*. This complicates the equations and makes them more difficult to balance.

When nitric acid acts upon zinc, zinc nitrate is formed, but the gas given off is not hydrogen. If the acid is concentrated, the liquid becomes hot, and torrents of red *nitrogen peroxide* escape:

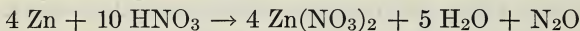


When nitric acid diluted with 5 times its volume of water is poured over zinc, zinc nitrate is formed as before, but the colorless gas that is evolved is *nitric oxide*:

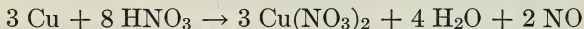


The nitric oxide, of course, passes into nitrogen peroxide as soon as it meets the oxygen of the air.

If the nitric acid is quite dilute and is kept cold, the product is chiefly *nitrous oxide*:



With other metals the equations are similar. Nitric acid rapidly acts upon copper, forming a green solution of copper nitrate. If the acid is dilute, nitric oxide is formed (§ 244):



On the other hand, if the nitric acid is concentrated, it becomes warm and nitrogen peroxide is formed:



Thus, when dilute nitric acid acts on copper, the gas in the lower part of the test tube is colorless, becoming red in the upper part where it meets the air, but if the acid is concentrated, a deep-red gas is formed throughout. Since the other familiar acids, when dilute, have little or no action on copper, this behavior serves as a convenient *test* for free nitric acid.

251. The nitrates. The nitrates are the salts formed when the hydrogen of nitric acid is replaced by metals. All of the nitrates are freely soluble in water. The three great industrial nitrates, those of sodium, potassium, and ammonium, have already been described. *Thorium nitrate*, $\text{Th(NO}_3)_4$, is a white solid largely used in the manufacture of gas mantles. *Silver nitrate*, AgNO_3 , is of great importance in photography, in medicine, and in the chemical laboratory.

NITRIC ACID IN INDUSTRY

252. Manufacture. The nitric acid that is required in great and increasing quantities by the chemical industries is made by two different methods:

1. *By the distillation of sodium nitrate (from Chile) with sulphuric acid.* The chemical change is the same as in the

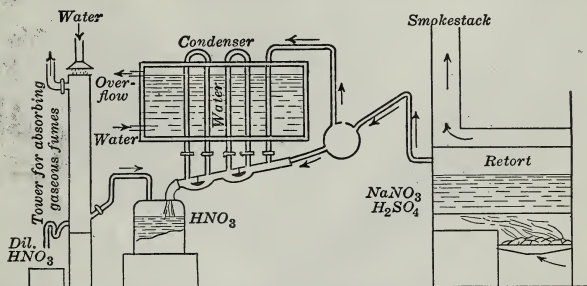
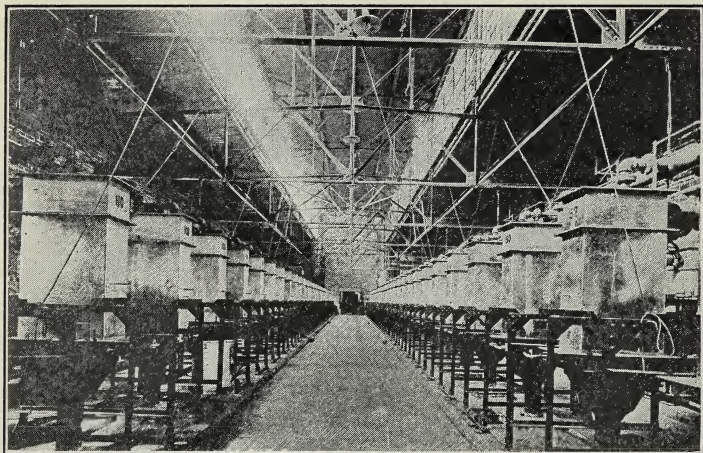
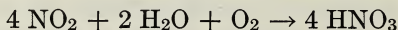


Fig. 126. Manufacture of nitric acid from sodium nitrate.

laboratory preparation of nitric acid (§ 246). The process is carried out in a horizontal cylinder of cast iron which is often large enough to take 20 tons of sodium nitrate and about an equal weight of sulphuric acid. The nitric-acid vapor that leaves the cylinder is condensed in a series of glass tubes which are kept cool by circulating water, and the liquid acid is collected in stoneware bottles or, in the newer plants, in vessels of *acid-proof iron* (§ 439).

2. *By the oxidation of ammonia with atmospheric oxygen* (the Ostwald process). The ammonia may be made from the nitrogen of air and the hydrogen of water, or it may be derived from gas works, from coke ovens, or from cyanamide. Whatever its source, it is mixed with 10 times its volume of purified air, and the mixed gases are passed rapidly through glowing platinum gauze, which is maintained at a temperature of 750° by means of an electric current.

Under the catalytic action of the platinum the ammonia is oxidized, the hydrogen to water, and the nitrogen to *nitric oxide*, NO, which, when the gaseous mixture is cooled, combines with more oxygen to form *nitrogen peroxide*, NO₂. Nitrogen peroxide interacts with water to form nitric acid:



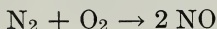
Courtesy of the Bureau of Ordnance.

Fig. 127. Catalyzers for the oxidation of ammonia to nitric acid at the United States Nitrates Plant at Muscle Shoals, Alabama.

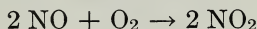
To bring about this interaction, the cold mixture of gases is passed upward through a brick tower 60 ft. high, packed with a porous, acid-proof filling down which water trickles. By the time it reaches the bottom, the water is converted into dilute nitric acid. The dilute acid is pumped from the bottom of this tower to the top of another similar tower, in which it is again subjected to the action of the gaseous mixture containing nitrogen peroxide. After 4 treatments of this kind the liquid contains 50 per cent of nitric acid, the balance being water. This solution can be concentrated, but the removal of the

water would bring the cost up to a point at which the concentrated acid could not compete with that made from sodium nitrate, which furnishes a concentrated acid *directly*. Hence ammonia gas is passed into the 50 per cent nitric acid, which is thus converted into *ammonium nitrate*. This finds a ready market in the explosives industry.

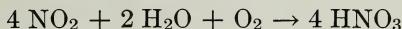
253. Nitric acid from air. The fixation of atmospheric nitrogen in nitric acid, by what is known as the Birkeland-Eyde process, is carried out chiefly in Norway. We have already mentioned the chemical changes that form the basis of it. When air is blown rapidly through a powerful electric arc, about 1 per cent by volume of nitric oxide is formed:



As soon as the gases become cool enough to permit the change, this nitric oxide will form nitrogen peroxide, for the gases that leave the arc still contain a large excess of oxygen:



As in the process just described, the current of gas containing nitrogen peroxide is then brought into intimate contact with water, whereupon nitric acid is formed:



Since much water is present when the nitric acid is produced, this interesting process, like the oxidation of ammonia, yields a dilute acid (50 per cent) for which there is little demand. In Norway this is treated with limestone, which is *calcium carbonate*, CaCO_3 , and converted into calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, which is marketed and used as a fertilizer under the name of "*air saltpeter*."

To maintain the great arcs, 6 ft. in diameter, that bring about the production of the nitric oxide from the air requires a lavish expenditure of electrical energy. Hence the process

cannot be carried profitably on where the dynamos that generate the current must be driven by engines. Cheap water power is essential to its success. This limits the field of the process, which shows little tendency to establish itself outside of Norway where water power is unusually abundant.

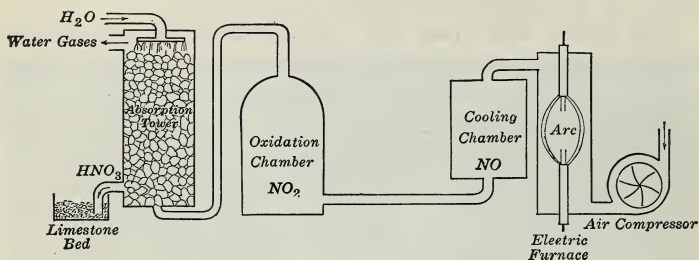


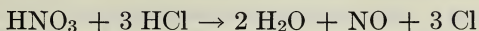
Fig. 128. Diagram of the Birkeland-Eyde process.

254. Uses. Nitric acid is an indispensable reagent in the laboratory of the chemist. Among its minor industrial uses are its employment in the manufacture of *liquid glue*, in *etching* the copper plates from which photographic illustrations are printed, and in making *silver nitrate*, *lead nitrate*, and other nitrates. Silk can be dyed yellow by cautious treatment with nitric acid, for silk, like wool, is a *protein*.

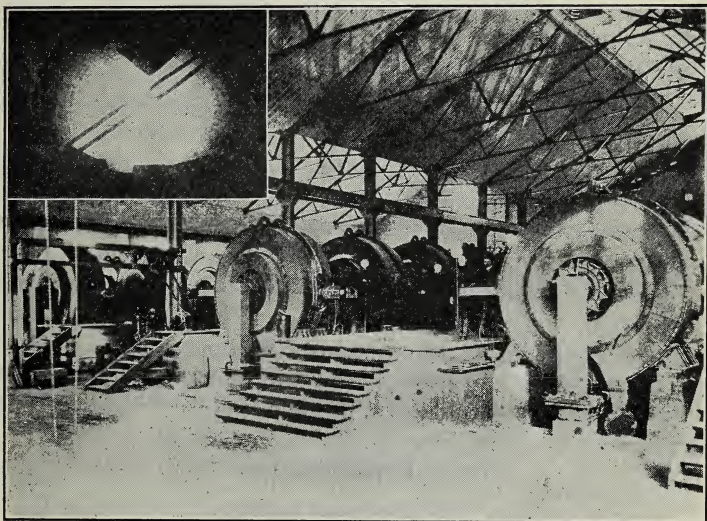
The main use of nitric acid is in the manufacture of explosives. Great quantities of it are consumed in making such important explosives as ammonium nitrate, tri-nitro-toluene ("T.N.T."), picric acid, nitroglycerine, guncotton, and smokeless powder. Because nitric acid is expensive to transport, large users find it best to make it themselves from sodium nitrate and sulphuric acid and even to establish lead-chamber plants and make their own sulphuric acid. The production of nitric acid in the United States is approximately 635,000 tons yearly.

255. Aqua regia. A mixture of nitric and hydrochloric acids in certain proportions is called **aqua regia**. It dissolves

gold and platinum, which are not acted on by either acid singly. The reason is that the nitric acid oxidizes the hydrogen of the hydrochloric acid to water, liberating chlorine:



The *nascent* chlorine converts the metal into a chloride, which is soluble in the water present. Thus, when aqua regia



Courtesy of the Norwegian Nitrogen Products Co.

Fig. 129. Birkeland-Eyde furnace plant at Notodden, Norway. Inset: the great disk of flame into which the arc is spread by electromagnets.

is employed to dissolve a noble metal, a solution of the *chloride*, not the *nitrate*, of the metal is obtained. Aqua regia is usually made by mixing 3 volumes of concentrated hydrochloric acid with 1 volume of concentrated nitric acid. Aqua regia is a strong oxidizing agent and rapidly destroys most organic substances.

SUMMARY

Nitrous oxide, N_2O , is the "gas" of the dentist. It is made by heating ammonium nitrate.

Nitric oxide, NO , is a colorless, poisonous gas produced when metals are acted upon by dilute nitric acid. In contact with air it instantly passes into red *nitrogen peroxide*, NO_2 .

Nitrogen peroxide is quite poisonous. In presence of air it interacts with water to form a solution of *nitric acid*.

Nitric acid, HNO_3 , is made (a) by distilling sodium nitrate with sulphuric acid; (b) by leading ammonia mixed with air through a hot platinum gauze; (c) by blowing air through a powerful electric arc. In both (b) and (c) the gases are cooled and brought into intimate contact with water, whereupon a 50 per cent solution of nitric acid is obtained.

Nitric acid does not affect gold or platinum and has only a slight action on aluminum. The other common metals are rapidly converted into nitrates. Nitric oxide or nitrogen peroxide escapes.

The most important use of nitric acid is in the *manufacture of explosives*.

Aqua regia is a mixture of nitric and hydrochloric acids in the proportion of 1 to 3 by volume. It converts into their chlorides gold and platinum, which are not attacked by either acid singly.

EXERCISES

1. How can nitric acid be obtained from air?
2. Mention two important sources of the nitric acid of commerce.
3. How does the behavior of nitric acid with metals differ from that of hydrochloric acid?
4. How many grams of nitrous oxide can be made by heating 20 grams of ammonium nitrate?
5. How many grams of pure nitric acid would contain 50 grams of oxygen?
6. Taking the specific gravity of pure nitric acid as 1.5, how many grams of oxygen do 3 liters of nitric acid contain?

7. How many kilograms of nitric acid can be obtained by heating with sulphuric acid (a) 200 kg. of sodium nitrate? (b) 200 kg. of potassium nitrate?

8. How many liters of nitrous oxide at 0°C . and 760 mm. can be obtained from 80 grams of ammonium nitrate?

9. How many grams of ammonium nitrate are needed to make 80 liters of nitrous oxide at 0°C . and 760 mm.?

10. How many grams of copper are needed to yield 30 liters of nitric oxide at 0°C . and 760 mm. when dissolved in nitric acid?

11. Sodium nitrate is cheaper than potassium nitrate, but if the two sold at the same price, which would be the more advantageous raw material for the production of nitric acid? With potassium nitrate the equation is: $\text{KNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HNO}_3$.

12. No nitrates of gold or platinum exist. How is it then that both metals dissolve in aqua regia?

13. In much of its chemical conduct nitrous oxide resembles oxygen. How could you distinguish the two by the aid of nitric oxide?

14. Assuming that air contains one-fifth of its volume of oxygen, how many liters of air will be required to interact with 1 liter of nitric oxide?

15. Why does nitric acid dissolve *silver* more readily than does hydrochloric acid? Why is nitric acid a better solvent for *lead* than is hydrochloric or sulphuric acid?

16. Why is the action of nitric acid upon the metals more complicated than that of hydrochloric or sulphuric acid?

REVIEW QUESTIONS

1. What is meant by an allotropic modification of an element?

2. What is *valence*? What is the valence of carbon in methane, CH_4 , and in carbon dioxide, CO_2 ?

CHAPTER XXV

CARBON (C = 12)

256. Occurrence. The important element **carbon** occurs native in a number of very different allotropic modifications. Two of these, **diamond** and **graphite**, are *crystalline*. Less pure, but in far greater abundance, carbon is found **amorphous**—that is, without crystalline form. The great deposits of **coal** on which civilization is founded are composed of impure amorphous carbon. **Coke, charcoal, and lampblack** are important manufactured forms of amorphous carbon.

257. Carbon compounds. The compounds of carbon are at once more numerous and more important to the welfare of mankind than those of any other element. The body of a man of average weight contains 25 lb. of carbon, so that 250 million tons of it are contained in the flesh and blood of the human race alone. Carbon in the form of carbon dioxide is disseminated through the atmosphere and is indispensable to the life of plants. Sugar and starch are nearly one-half carbon by weight, and all food products, and, in fact, all animal and plant substances, are composed of carbon compounds. The blackening or charring that occurs when such materials are overheated in cooking is due to the formation of amorphous carbon, so that the mere application of heat serves as a *test* for the presence of carbon in food products.

Among other important materials containing carbon may be mentioned *oils, fats, waxes, soap, and rubber*. Many of our most important *drugs*, and all *dyestuffs, perfumes, and photographic developers* are carbon compounds. One hundred pounds of *marble* contain 12 pounds of carbon, and many other important minerals are compounds of this element.

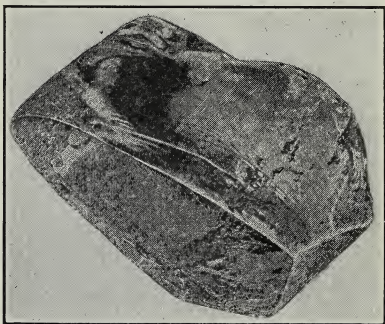
258. Diamond. Some diamonds are found in gravel deposits in India, Brazil, Borneo, and in the Ural Mountains, but practically all of the output of the gems now comes from the Kimberley district, in the Cape Province, Union of South Africa. The most productive of the Kimberley mines could all be included within a small circle $3\frac{1}{2}$ miles in diameter. Out of this little area has come perhaps a billion dollars' worth of gems.

The largest diamond ever obtained was the "Cullinan," which was found in the Premier mine in 1905 and which was presented to King Edward VII of Great Britain on the 66th anniversary of his birth. It weighed, before cutting $3,034\frac{3}{4}$ carats, which is more than 1 lb. 5 oz. avoirdupois, and yet its shape when found showed clearly that it was only a part of what was originally a much larger crystal.

The color of natural diamonds varies in different specimens from white through yellow and brown to black. Only pink, blue, or colorless stones are esteemed as gems. Even a slight tint of yellow detracts greatly from the value. The diamonds worn as gems are not crystals. They are *brilliants*, cut in such a way as to display the "fire" to the best advantage.

Black diamonds, most of which come from Bahia, Brazil, are largely used as an abrasive for glass cutting, for the cutting surfaces of rotary rock drills, and the like.

The diamond is the densest form of carbon, its specific gravity being 3.5. Its lustre is due to its enormous power of refracting light and also to the fact that its refracting power is very different for light of different colors, so that at one angle



Courtesy of Tiffany & Co.

Fig. 130. Model of the Cullinan diamond, reduced one-half.

the eye receives a glint of red, at another, one of green, and so on. Diamond is the hardest of minerals, and it can be cut and

polished only by diamond dust. It is a non-conductor of electricity and a poor conductor of heat.

Diamond is chemically inactive, and it is not at all affected by any liquid at ordinary temperatures. When heated in a vacuum to a very high temperature, it turns black, swells up, and is converted into a mass resembling coke.

In oxygen diamond takes fire at a white heat and burns brilliantly, yielding carbon dioxide which is identical in all respects with that obtained by burning the other modifications of carbon.

Diamonds have been made from charcoal by the great French chemist *Moissan*.

Moissan heated in a crucible a mixture of charcoal powder and iron to $3,000^{\circ}\text{C}.$, by means of the electric arc (Figure 132). When the boiling liquid iron had dissolved some of the charcoal, the crucible was taken out of the furnace and plunged into water. The result of the sudden cooling was to form a crust of solid iron on the surface, which

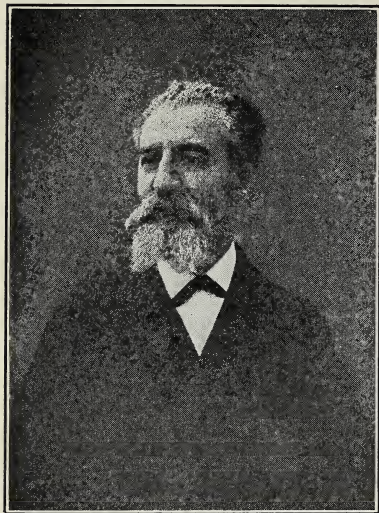


FIG. 131. HENRI MOISSAN (1852-1907).

French chemist, professor of chemistry in the Sorbonne, University of Paris; investigated the behavior of many substances at high temperatures in the electric furnace; discovered calcium carbide, melted and vaporized lime, and made diamond artificially; first isolated fluorine.

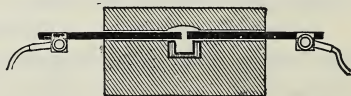


Fig. 132. Moissan's electric crucible furnace.

exerted a powerful pressure on the liquid interior. When the iron was dissolved away by acids, it was found that some of the charcoal had been converted into little diamonds. Their small size (0.5 mm. in diameter) renders them of no commercial value.

259. Graphite. Deposits of graphite, also called **plumbago** and **black lead**, occur in Massachusetts, New York, Pennsylvania, and elsewhere in the United States and Canada. Much graphite comes from Ceylon and from the mines of eastern Siberia.

Graphite is found in flat hexagonal crystals and also in large masses which have no distinct crystalline form. It has a blackish-gray metallic lustre, and, like lead, it leaves a black mark on paper. Unlike the diamond, graphite is one of the softest of minerals, being greasy to the touch and easily scratched by the finger nail. Since its specific gravity is only 2.25, it is far less dense than the diamond, from which it differs also in being a conductor of the electric current.

Graphite is inactive chemically, being quite unaffected by all ordinary reagents. It is somewhat soluble in melted iron. At a very high temperature it combines slowly with oxygen to form carbon dioxide.

Like diamond and charcoal, graphite has *never been melted*. This property causes it to be largely used where extreme resistance to heat is needed. Crucibles for melting metals are made of a mixture of equal parts of fireclay and graphite. They resist heat better than crucibles made of clay alone, and they are more economical of fuel since graphite is a much better conductor of heat than clay. The large electrodes that carry the current into and out of electric furnaces are made of graphite.

The "lead" of pencils is a mixture of powdered graphite with fine clay freed from grit. The hard pencils contain less graphite and more clay than the soft.

Graphite makes an excellent gray-black *paint*. It is much

employed as a *lubricant*. *Stove polish* is made of graphite and soap.

Graphite is not restricted to the earth alone. It has often

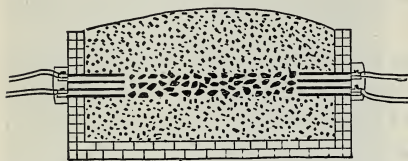


Fig. 133. Manufacture of artificial graphite.

vapor is carried some distance outward and reaches a place where the temperature is not quite so high, condensation occurs and a white-hot cloud of graphite crystals results. Much of the radiance of the sun is due to these incandescent clouds of graphite.

260. Artificial graphite.

Large quantities of graphite are made at Niagara by heating anthracite coal in the furnace shown in Figure 133. The furnace is 15 ft. long. The side walls are made of loose blocks which can be taken down to remove the charge. The coal is used in small lumps, and since it is almost a non-conductor of electricity,

there is placed between the electrodes, to carry the current, a core of small pieces of a dense, conducting variety of carbon

been found in the meteors which come to us from space. Since the temperature of the surface of the sun is $6,200^{\circ}\text{C}.$, carbon exists in its atmosphere as a *vapor*.

When a mass of carbon

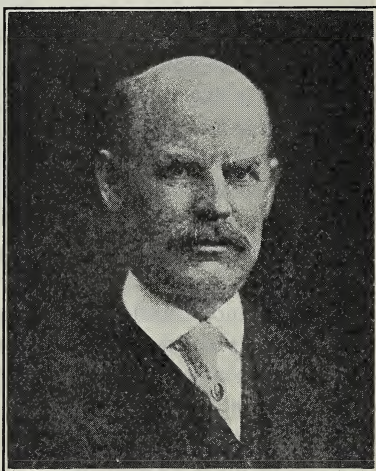
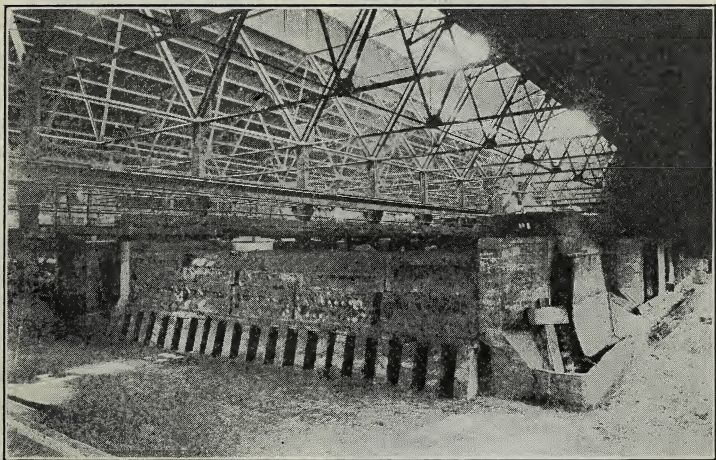


FIG. 134. EDWARD GOODRICH ACHESON (1856-).

American chemist and inventor; discovered and developed processes for the manufacture of graphite, carborundum, and other products of the electric furnace.

obtained from gas works. The whole is covered with a mixture of sand and powdered coal to exclude the air. The run lasts 20 hours, during which the intense heat generated in the core penetrates the charge, vaporizes the impurities of the coal, and transforms its carbon into graphite which is purer

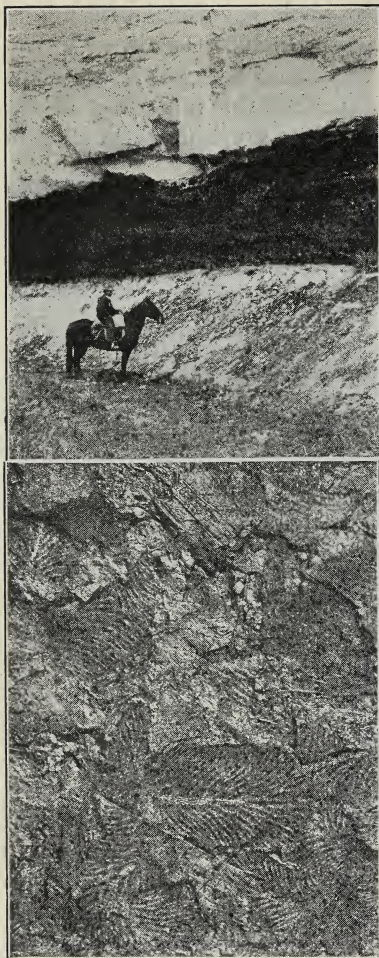


Courtesy of the Acheson Graphite Co.

Fig. 135. Artificial graphite furnace in operation.

than that found in nature. Electrodes, crucibles, and other objects are moulded of powdered coal and then "graphitized" in a similar furnace.

261. Coal. In the geological history of the earth there was a period, called the *Carboniferous period*, in which vegetation was far more luxuriant than it is at present because the temperature was higher and the air richer in carbon dioxide. Over vast marshy plains not far above sea level grew forests of a richness and density of which a tropical jungle of the present day gives only a faint idea. Leaves, branches, and trunks lay where they fell, and immense masses of vegetable debris were accumulated, which were later covered with earth and con-



Courtesy of the U. S. Geological Survey.

Fig. 136. Occurrence and origin of coal: above, outcrop of a Montana lignite bed; below, fern imprints in Illinois bituminous coal.

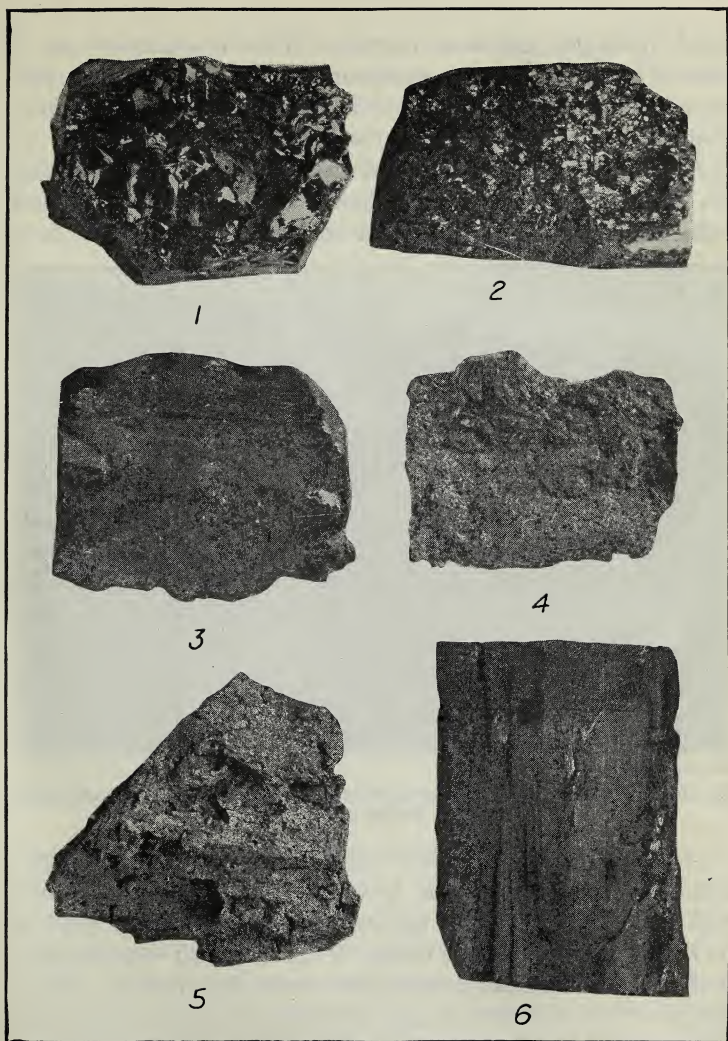
verted into **coal** by a slow change in which warmth and the pressure of overlying rocks played an important part.

Vegetable matter—wood, for instance—contains mostly carbon, hydrogen, and oxygen. Its conversion into coal consists in the removal of the last two elements with a portion of the carbon, the rest of the carbon being left, with all of the mineral matter of the original plant, as coal. This process is very gradual, and all stages of it are found in nature. The following are examples:

1. **Peat** is plant substance only slightly carbonized and still retaining a distinct vegetable structure.

2. **Lignite** is a brown, imperfect, and woody coal, found in the newer rocks.

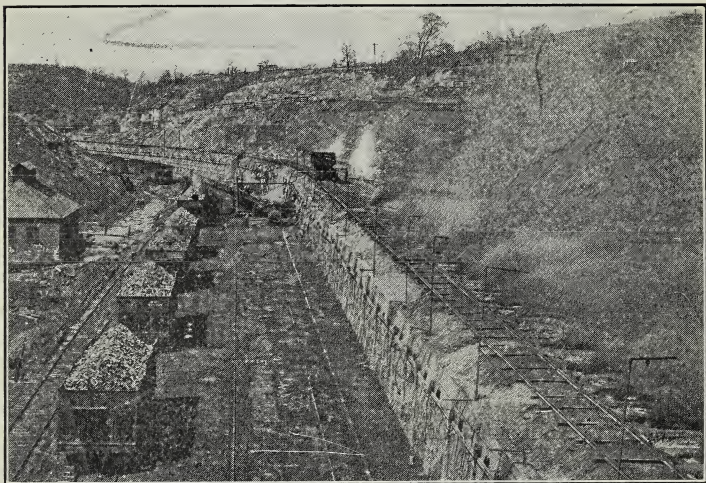
3. **Bituminous coal**, often called **soft coal**, has a dull greasy or pitchy lustre. It is less dense than *anthracite*, more fragile, and takes fire more readily. Bituminous coal still contains



Courtesy of the Philadelphia Commercial Museum.

Fig. 137. Six carbon fuels: 1, anthracite coal; 2, bituminous coal; 3, lignite; 4, peat; 5, coke; 6, charcoal.

much hydrogen and some oxygen. When it is heated out of contact with air, gaseous compounds of hydrogen and carbon escape which burn with a bright flame, while in the vessel there remains a grayish-black residue called **coke**, composed of carbon with some mineral matter. *Coal gas* or *illuminating gas* is made by heating bituminous coal in closed *retorts* and collecting the gas given off in gas holders.



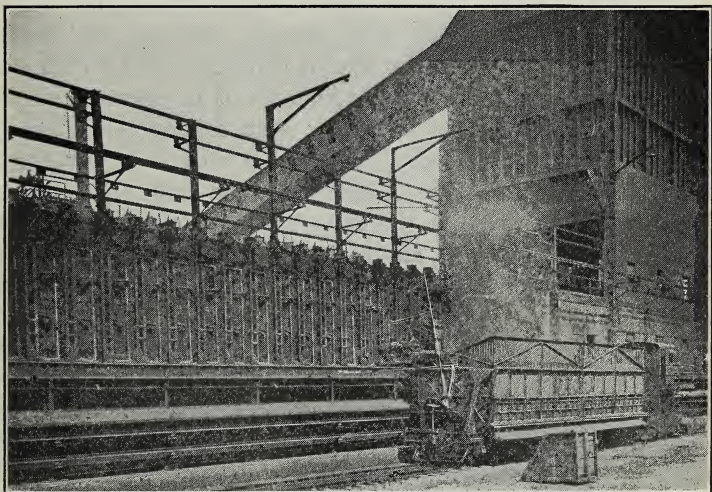
Courtesy of the Hillman Coal & Coke Co.

Fig. 138. A battery of modern beehive coke ovens, mechanically charged and discharged.

4. **Anthracite coal**, often called **hard coal**, has a bright, almost metallic, luster. It is tougher and denser than soft coal and more difficult to ignite. Anthracite has lost most of its hydrogen. It consists chiefly of carbon, with some mineral matter, which remains as **ash** when the coal is burned. When heated in the absence of air, anthracite is almost unaltered, and little gas escapes. As a domestic fuel anthracite is greatly superior to soft coal, but it is far less abundant and is available only in favored localities.

5. **Graphite**, which contains no hydrogen and which is so difficult to burn that it could not be used as fuel even if it were sufficiently abundant, is the final product of the change.

262. Coke. Coke bears the same relation to soft coal that **charcoal** does to wood. It is made by heating soft coal out of contact with air until everything that can be driven off by heat has escaped. Such a process is known as **destructive**



Courtesy of the U. S. Steel Corporation.

Fig. 139. A battery of by-product retort coke ovens with coke quenching car.

distillation. The older coking process, still much used in this country, employed dome-shaped *beehive ovens*, in which the heat was generated by the burning of part of the coal charge, and the gases produced were allowed to escape. The modern process uses closed ovens containing *retorts* about 30 ft. long, 6 ft. high, and $1\frac{1}{2}$ ft. wide, which are heated from the outside by numerous Bunsen flames. The furnaces are made narrow so that the heat can penetrate to the center of the mass of coal. The flames are fed with the gas from previous charges, which

is stored in gas holders for the purpose. The valuable volatile *by-products* which are formed are led away from the furnace through pipes and purified.

When the conversion of the coal into coke is complete, the coke is pushed out of the oven by a powerful piston, operated by hydraulic pressure, and immediately quenched with abundant water. Among the *by-products* recovered are *illuminating gas*, *ammonia water*, *benzene*, *toluene*, *naphthalene* (often called "*tar camphor*"), *carbolic acid*, *creosote*, *coal tar*, and *pitch*. The process yields more gas than it consumes, and millions of cubic feet of gas are sold daily from the coke ovens to neighboring towns. Creosote is largely used to impregnate wood for protection against decay, coal tar has proved its value as a road binder, and benzene, toluene, carbolic acid, and naphthalene are indispensable to the manufacture of drugs, dyestuffs, photographic developers, and high explosives.

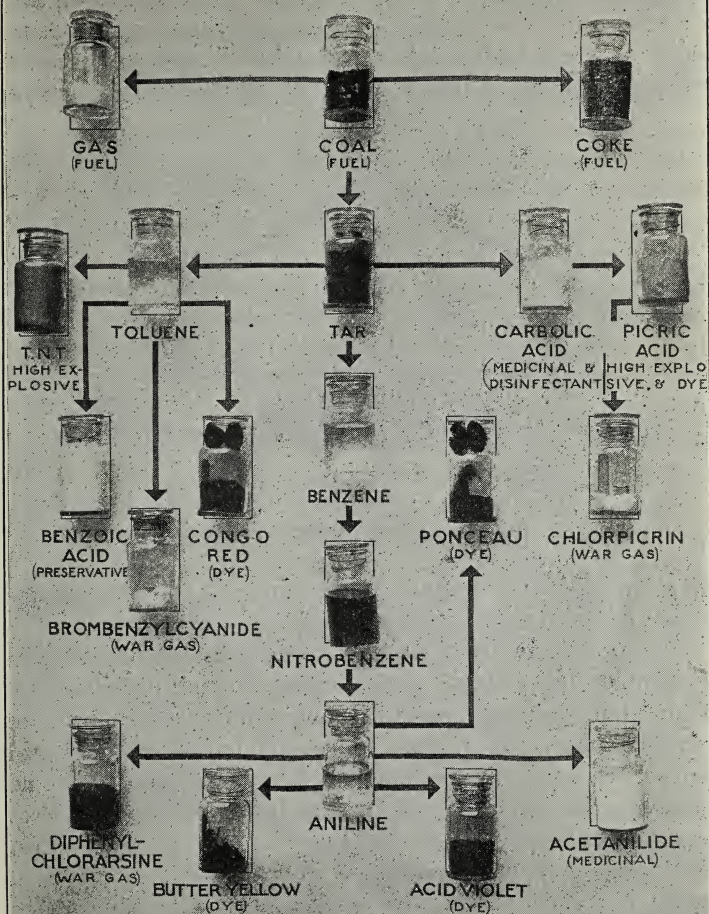
Coke is the great fuel of the iron industry; it is made in enormous quantities for use in the blast furnace.

Oil coke is the residue left in the iron cylinders in which *petroleum* is distilled. It resembles ordinary coke but is purer, being almost free from mineral matter and therefore leaving very little ash when burned. It is an excellent fuel when high temperatures are desired.

263. Manufacture of charcoal. Charcoal is made from wood by heating in the absence of air. Billets of wood are loaded into iron cars and run into a large cylinder made of boiler plate and equipped with rails (Fig. 141). The cylinder (*A*) is heated from the outside, and the cars remain in it during the distillation. The vapors that are formed are led through pipes to condensers (*B, B*), where a liquid collects from which some valuable *by-products* are obtained. The most important of these are *wood alcohol*, CH_4O (§ 588), *acetone*, $\text{C}_3\text{H}_6\text{O}$ (§ 608), and *acetic acid*, $\text{C}_2\text{H}_4\text{O}_2$ (§ 596). The combustible gases that are not liquefied in the condensers go back to the furnace and are burned under the cylinder to assist in the heating.

COAL PRODUCTS

IN WAR AND PEACE TIME INDUSTRIES



Courtesy of the National Research Council.

Fig. 140. Typical products derived from coal.

264. Properties of charcoal. Charcoal is not pure carbon. It still contains some hydrogen and oxygen, as well as 1.5 per cent of mineral matter. Its properties depend upon the temperature applied in its manufacture. Charcoal made at a low temperature is dead-black or brownish and highly inflammable, whereas high temperature yields a charcoal which is gray-black, dense, a better conductor of the electric current,

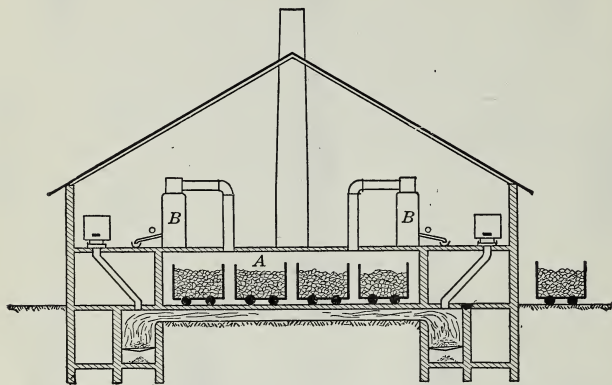


Fig. 141. A modern charcoal plant.

and more difficult to ignite. At the temperature of the electric furnace charcoal passes without melting into graphite.

The specific gravity of charcoal varies from 1.5 to 2 in different samples, but because of its porous structure it floats upon water. For the same reason it has a remarkable power of absorbing gases. If a dead mouse be buried in powdered charcoal, no odor of putrefaction will be perceived, for all the offensive gases produced will be absorbed. Charcoal made of cocoanut shells will take up 200 times its volume of ammonia. Respirators containing powdered charcoal afford protection against many poisonous gases, and a layer of charcoal made from nut shells was an important part of the gas masks used in the World War.

The distillation of wood to obtain charcoal and the by-products, wood alcohol, acetone, and acetic acid, is an important industry. In Sweden alone 1,000,000 tons of charcoal is made annually, all of which is used in the production of high-grade steel for tools and cutlery.

265. Boneblack. Boneblack, or **animal charcoal**, is made by charring bones in an iron cylinder from which air is excluded. It is a black, granular substance which contains only one-sixth of its weight of carbon, the balance being the mineral matter of the bones. The most important property of boneblack is its remarkable power of absorbing colored impurities from liquids. This can be illustrated by coloring water with a little litmus and then boiling with boneblack, whereupon the fluid becomes colorless. In the refining of sugar the brown "raw" sugar is dissolved in water and the brownish syrup filtered through a layer of boneblack 20 ft. in depth. The boneblack retains all the coloring matter, so that when the syrup is evaporated until the sugar separates in crystals, the familiar *white* sugar of the household is obtained. Powdered boneblack is also used in shoe polish and as a black paint.

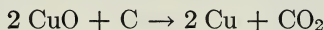
266. Lampblack. Lampblack is merely pure *soot*. When a cold porcelain plate is held in a candle flame, lampblack deposits. On a large scale the best grade of lampblack, called **carbon black**, is often made by a method in principle the same. Flames fed with natural gas are allowed to burn against the lower surface of a revolving cast-iron vessel which is kept full of running water to cool it. As the lampblack collects, a scraper automatically removes it. Lampblack is also made by burning substances like rosin, turpentine, or petroleum with an inadequate supply of air so that much soot is produced. The smoke is led through chambers in which the lampblack is deposited on the walls or on cloths hung up to receive it.

Lampblack is a velvety, jet-black powder which shows no trace of crystallization. Its specific gravity is 1.8. The temperature of the electric furnace transforms it into graphite.

It is used in the manufacture of printers' ink, India ink, and shoe polish. Since lampblack is entirely unaffected by the weather, it makes excellent black paint. Its largest use is as a "filler" in the manufacture of automobile tires.

267. Chemical conduct of carbon. At ordinary temperature carbon is inert, showing little or no tendency to unite with other elements. For this reason fence posts are often charred before they are inserted in the soil. The layer of inert carbon on the surface protects the wood from the chemical changes that lead to decay and disintegration. At high temperatures, however, carbon burns in the air to *carbon dioxide*, CO_2 , if the air supply is plentiful; if the air access is limited, more or less *carbon monoxide*, CO , is produced.

Carbon not only combines with free oxygen, but it removes the oxygen from most oxides when heated with them. Thus, when black *copper oxide* is heated with powdered charcoal, coke, or anthracite, *carbon dioxide* escapes, and a red powder of copper remains:



At the temperature of the electric furnace carbon combines with many metals, forming **carbides**. The most important of these compounds is *calcium carbide*, CaC_2 , which will be described later.

The universal use of amorphous carbon as **fuel** is based on the following facts:

1. Carbon in the form of coal or coke is *cheaper* than any other suitable material.

2. Carbon when burned liberates over 8,000 calories of heat per gram. This means that a given weight of carbon, burned with perfect efficiency, would heat 8,000 times its weight of water 1°C . A pound of good coal produces over 14,000 British thermal units (B.t.u.) of heat. Far more energy can be obtained from a pound of coal, coke, or charcoal than from a pound of dynamite, nitroglycerine, or guncotton.

3. The product of combustion of carbon is a *gas*, which is automatically removed by the draft and discharged into the air. Even if cheap enough, an element that formed a *solid* oxide could hardly be employed as fuel, since the oxide would at once clog the furnace and make it impossible to maintain the combustion.

SUMMARY

PROPERTIES OF CRYSTALLINE CARBON

	Diamond	Graphite
<i>Color</i>	Colorless	Gray-black
<i>Lustre</i>	Brilliant	Metallic
<i>Transparency</i>	Transparent	Opaque
<i>Crystalline form</i>	Well developed	Imperfect
<i>Hardness</i>	Hardest of minerals	Very soft
<i>Specific gravity</i>	3.5	2.25
<i>Electrical conductivity</i>	Non-conductor	Good conductor
<i>Ignition point</i>	850°	700°

PROPERTIES OF AMORPHOUS CARBON

	Anthracite Coal	Bituminous Coal	Coke	Charcoal	Lampblack
<i>Lustre</i>	Bright, almost metallic	Pitchy	Gray, semi-metallic	Dull black	Velvety black
<i>Tenacity</i>	Tough	Fragile	Tough	Fragile	None
<i>Specific gravity</i>	1.5	1.3	2	1.5	1.8
<i>Volatile matter</i>	5 per cent	35 per cent	Traces	Traces	Traces
<i>Effect of heat in absence of air</i>	Almost unchanged	Forms coke	Unchanged	Unchanged	Unchanged
<i>Flame</i>	Blue	Smoky yellow	Blue	Blue	Blue
<i>Ash</i>	10 per cent	8 per cent	10 per cent	1.5 per cent	None

Carbon is inert in the cold, but when heated to redness it combines energetically with oxygen and removes the oxygen from many metallic oxides. For this purpose it is the cheapest substance available and is used in large quantities.

EXERCISES

1. Compare the properties and uses of the crystalline allotropic modifications of carbon.

2. What is the evidence that the different forms of carbon are composed of the same element?

3. Summarize the distinctions between anthracite and bituminous coal.

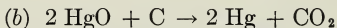
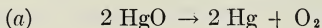
4. Describe the manufacture of coke. Mention the chief by-products, with their uses.

5. How is the destructive distillation of wood conducted? What are the chief by-products?

6. Compare the properties of charcoal with those of coke.

7. What is the action of red-hot carbon on metallic oxides?

8. Mercuric oxide is heated (*a*) alone, (*b*) with carbon, (*c*) in hydrogen. Calculate the number of grams of all the products in each case if 10 grams of mercuric oxide were used.



9. Your body contains about 25 lb. of carbon. What was the original source of this carbon? Trace the stages through which the carbon has passed. What will be its future?

10. Describe the manufacture of artificial graphite. How could you distinguish it from natural graphite?

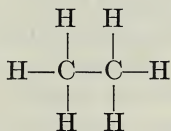
11. How could you distinguish anthracite from bituminous coal?

CHAPTER XXVI

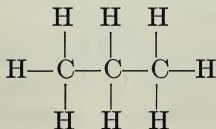
THE SIMPLER COMPOUNDS OF CARBON

268. Carbon compounds. The compounds of carbon are far more numerous than those of all the other elements taken together. This is due to the fact that the atoms of carbon have a power, not shared by those of the other elements, of uniting with *each other*. Take, for instance, the compounds of carbon with hydrogen. The valence of carbon is 4, and therefore the *simplest* compound that it forms with hydrogen has the formula CH_4 . This is **methane**, commonly called **marsh gas**.

However, not only does a single atom of carbon form a hydrogen compound, but there is a second compound, called **ethane**, in which 2 atoms of carbon are linked together, each being also united to hydrogen atoms. The arrangement of the atoms in the molecule of ethane is indicated by the graphic formula:



In a third compound, **propane**, a chain of 3 carbon atoms exists, each of which also carries hydrogen atoms:



There is no definite limit to this linkage of the carbon atoms.

A compound containing a chain of 60 linked carbon atoms, each being also in union with atoms of hydrogen, has been obtained. The same power of forming chains extends to the compounds of carbon with elements other than hydrogen. This peculiar power of the carbon atoms explains the fact that *more than 150,000 compounds of carbon are known*. A few of the simpler and more important of these compounds will be taken up at this stage. Some more complicated carbon compounds which have important uses will receive attention in Chapters XL-XLIII.

CARBON DIOXIDE, CO_2

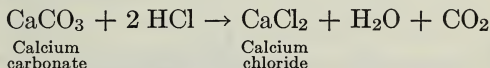
269. Occurrence. The small percentage of carbon dioxide in the atmosphere and its connection with the life of plants have already been discussed. Far richer in carbon dioxide than ordinary air is the air that fills the pores of the *soil*. This contains from 1 to 12 per cent of carbon dioxide, derived from decomposing vegetable matter. It is this air that is responsible for cases of suffocation in wells and other excavations. Thus carbon dioxide is constantly given off from fertile soil, and this forms an important source of the gas for plants. The weight of carbon dioxide that escapes from an acre of good land during a summer has been estimated at 6 tons.

Carbon dioxide is contained in the gases emitted from volcanoes, and it sometimes appears at points miles distant from the seat of volcanic disturbance. After an eruption of Vesuvius carbon dioxide has occasionally escaped from the soil in sufficient quantity to suffocate hundreds of small animals, while at the same time the cellars in Naples, 10 miles from the crater, became filled with the gas.

Near Naples is a cave called the *Grotto del Cane*, which has a depression about 2 ft. deep in the floor. This sunken portion is kept full of carbon dioxide by a natural outflow. Dogs that venture into it are suffocated, but a man walks about unharmed because his head is above the level of the dense gas. *Death*

Valley in Java is a little wooded hollow in which many wild animals are killed in the same way. Some of the gold mines at Cripple Creek, Colorado, are subject to sudden outbursts of carbon dioxide from the rocks, which have, at different times, caused the deaths of a hundred miners. Carbon dioxide is the “choke damp” or “black damp” of the coal miner.

270. Preparation. Carbon dioxide is prepared in the laboratory by the action of hydrochloric acid on marble, which is *calcium carbonate*, CaCO_3 :



The apparatus is the same as that shown in Figure 67. The gas is collected by downward displacement.

271. Physical properties. Carbon dioxide is a colorless gas, and it is odorless when diluted with air. When concentrated carbon dioxide has a pungent odor. Above 31°C ., which is its *critical temperature*, no pressure, however great, will liquefy it. At room temperature it is converted by a pressure of 54 atmospheres into a colorless liquid, which freezes to a mass resembling snow when the pressure is removed.

From the formula CO_2 the molecular weight of carbon dioxide is 44. Hence its specific gravity referred to air must be $\frac{44}{29}$, or about 1.5. This high density is strikingly shown by allowing a soap bubble to fall into a large jar in which carbon dioxide is being generated by the action of hydrochloric acid on marble. The bubble floats on the surface of the dense gas as though borne up by an invisible liquid (Fig. 142). The same property of the gas is shown by the experiment of Figure 143. The upper vessel contains carbon

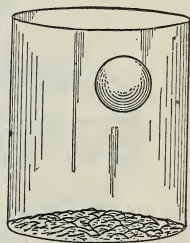


Fig. 142. A soap bubble floats on carbon dioxide.

dioxide, which is allowed to flow down one side of a trough in which several candles are burning at different levels. Beginning with the highest on that side, the candles are extinguished in order as the dense gas reaches the flames. When it reaches the bottom of the trough, the gas rises on the other side, extinguishing the candles on that side in order beginning with the lowest. The fact that carbon dioxide is

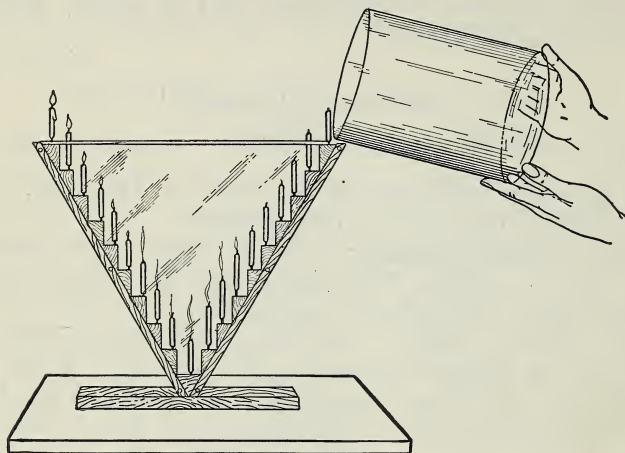


Fig. 143. Carbon dioxide can be poured as though it were a liquid.

so much denser than air explains its tendency to run, almost like a liquid, into excavations and to remain there until gradually removed by diffusion into the air.

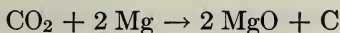
At ordinary temperature and pressure water dissolves its own volume of carbon dioxide. The same statement holds good if the pressure be doubled. The water will still dissolve its own volume of the compressed gas, but since, according to Boyle's Law, any gas is made twice as dense by doubling the pressure upon it, the *weight* of carbon dioxide forced into the water is twice as great as before. **Soda water** is water that has been made to dissolve compressed carbon dioxide. In pre-

paring 100 liters of soda water, 300 liters of carbon dioxide are compressed to 100 liters by a pressure of 3 atmospheres and then dissolved in 100 liters of water. When this liquid is allowed to run into a glass, the pressure is suddenly reduced from 3 atmospheres to 1, and two-thirds of the dissolved gas escapes in bubbles, causing the *effervescence*. In the same way the effervescence of bottled beverages is due to carbon dioxide dissolved in the liquid under pressure, which partially escapes when the pressure is reduced by opening the bottle.

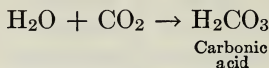
We have seen (§ 223) that in ascertaining whether ventilation is good or bad it is usual to be guided by the percentage of carbon dioxide in the air of the room. This is not because the gas is poisonous, but merely because its percentage is a good *index* of the degree of purity of the air. In fact, carbon dioxide cannot be ranked as a poisonous gas. The effects of increasing amounts in air are given below:

Per cent CO ₂ by Volume	Effect
2	No marked discomfort
3	Candle extinguished
4	Deep breathing, increasing to panting on muscular effort; quick fatigue
10	Distress, headache, flushed face, incipient stupefaction
12-15	Unconsciousness; death on prolonged exposure

272. Chemical conduct. The oxygen atoms of carbon dioxide are firmly held in the molecule, and it acts like water on almost all flames, even on that of burning phosphorus, extinguishing them by excluding oxygen. Its connection with the working of the chemical fire extinguisher has been referred to. Burning magnesium, however, continues its brilliant combustion in carbon dioxide, while carbon, in the form of soot, deposits on the walls of the vessel:



The solution of carbon dioxide in water colors blue litmus faintly *red* and forms salts with bases. It contains carbonic acid, H_2CO_3 , formed thus:



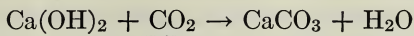
Carbonic acid, a very feeble acid, is known only in solution, but its salts, the **carbonates**, are of great industrial importance. *Sodium carbonate*, Na_2CO_3 , and *potassium carbonate*, K_2CO_3 , have been described. *Calcium carbonate*, CaCO_3 , occurs in more or less impure condition as **marble** and **limestone**. It is one of the commonest of minerals; with *magnesium carbonate*, MgCO_3 , it forms whole mountain ranges in some localities. The carbonates of lead, copper, and iron are important ores of the corresponding metals. Many other carbonates are found as minerals.

Since the air in the soil is rich in carbon dioxide, the water in the soil becomes charged with carbonic acid, which gives it a refreshing flavor, noticeable in good spring water. The flat taste of boiled water is due to the fact that its dissolved gases have been expelled by boiling, and it no longer contains carbonic acid.

The carbonic acid in the soil water plays an important part in the nutrition of plants. Soluble potassium compounds are essential to plant life. Potassium is abundant in the rocks, but it is locked up in insoluble compounds (silicates) and is useless to plants. Carbonic acid slowly converts the insoluble potassium compounds into *potassium carbonate*, which is soluble in water and available as plant food. Thus the supply of soluble potassium compounds in the soil is slowly but constantly replenished.

273. Test for carbon dioxide. The transparent liquid **limewater** is a saturated solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$. In contact with carbon dioxide the liquid becomes milky from

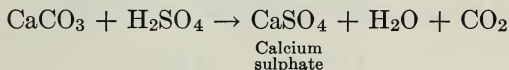
the formation of a white precipitate of *calcium carbonate*, CaCO_3 :



An excess of carbon dioxide will redissolve the precipitate and again make the liquid clear. Hence the whole progress of the test must be carefully watched to avoid error.

274. Carbon dioxide in industry. Carbon dioxide is a by-product of the fermentation that produces grain alcohol, and the gas that collects in the fermenting vats is often drawn off through pipes and liquefied in cylinders for the market.

In some localities where large quantities of carbon dioxide issue from the earth ("gas springs"), it is collected and utilized. Carbon dioxide is also made on a large scale by various chemical methods, one of which is the action of sulphuric acid on marble dust:



Carbon dioxide appears in commerce in strong steel cylinders which contain it as a liquid under a pressure of over 50 atmospheres. When a cylinder is inverted and the valve opened, the liquid rushes out, and a portion of it evaporates so rapidly and absorbs so much heat that the remainder of the liquid is frozen to *solid carbon dioxide*, which looks like snow but is much colder, having a temperature of -80° . It is convenient to tie a cloth bag over the outlet of the inverted cylinder. When the valve is opened, the bag rapidly fills with a snowy mass of solid carbon dioxide.

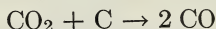
275. Uses of carbon dioxide. Solid carbon dioxide serves as a convenient refrigerant in the laboratory when very low temperatures are desired, but the main commercial use of the cylinders is in "carbonating" beverages, that is, charging them with carbon dioxide. Shells filled with liquid carbon dioxide have been used in warfare for disabling tanks. A tank is moved

by a gasoline engine which requires a constant supply of oxygen. The bursting of such a shell close at hand fills the engine with carbon dioxide and stops it, reducing the tank to a condition in which the opposing artillery can readily destroy it.

The importance of the carbon dioxide of the air to plants and the work of the carbonic acid of soil water in rendering plant food available have been discussed. The part played by carbon dioxide as a leavening agent has been mentioned in connection with baking powder. When *yeast* is used, the carbon dioxide that makes the bread light and porous is produced by *fermentation* instead of by the interaction of chemicals.

CARBON MONOXIDE, CO

276. Preparation. When carbon dioxide is slowly passed through an iron tube packed with lumps of charcoal and heated in a furnace, **carbon monoxide** is produced:



This formation of carbon monoxide by the action of glowing carbon upon carbon dioxide is of great importance both in industry and in the house-

hold. For the laboratory a more convenient mode of preparation has been devised. *Formic acid*, CH_2O_2 , is a colorless liquid, which, when mixed with warm concentrated sulphuric acid, gives a regular current of pure carbon monoxide which can be collected over water (Figure 144):

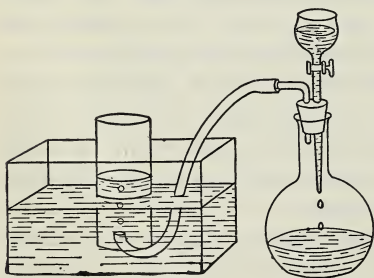
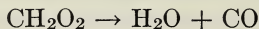


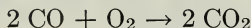
Fig. 144. Preparation of carbon monoxide from formic acid.



Only the formic acid is decomposed. The sulphuric acid aids the chemical change by reason of its intense attraction for water.

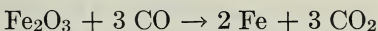
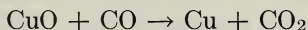
277. Physical properties. Carbon monoxide is a colorless, odorless, poisonous gas. It has been liquefied and solidified at very low temperatures. As the formula shows, its specific gravity is the same as that of nitrogen, and it is, therefore, a trifle lighter than air. Its solubility in water also is about the same as that of nitrogen, 40 volumes of water being required to dissolve 1 volume of carbon monoxide under ordinary conditions.

278. Chemical conduct. Carbon monoxide burns in air or in oxygen with a hot, blue, almost non-luminous flame to form carbon dioxide:



The blue flame which can be seen on the surface of a coal fire is due to burning carbon monoxide.

At a red heat carbon monoxide removes the oxygen from many oxides of the metals:



This behavior of carbon monoxide is of the utmost importance in the extraction of metals from their ores. Practically all of the iron of the world is made by the action of carbon monoxide on iron oxide.

279. Carbon monoxide as a poison. Carbon monoxide is called "white damp" by the miner. It is one of the most frequent causes of fatalities in coal mines. Cases of suffocation due to its presence in the air of ordinary dwellings are not at all unusual. Hence the subject of its action upon the body is one of great practical interest.

A man sitting quietly and breathing air containing 0.1 per cent of carbon monoxide would become insensible in 2 hours and would die shortly thereafter. Muscular exertion increases

the amount of the gas inhaled and brings about prostration in 30 minutes or thereabout. For air containing 0.2 per cent of carbon monoxide the times just given must be divided by 2, and so on. Large percentages of the gas in air are quite sudden in their effects.

Small birds, especially canaries, quickly show the symptoms of carbon-monoxide poisoning and render valuable assistance in investigating suspicious atmospheres in mines and elsewhere. In air containing 0.2 per cent of carbon monoxide a canary shows marked distress in $1\frac{1}{2}$ minutes and falls from its perch in 5 minutes. Rescuing parties in mines carry small cages containing canaries; when the birds begin to suffer, the unprotected miners return, and only those equipped with oxygen helmets proceed further.

The oxygen of the blood is carried about the body in the red blood corpuscles. These contain oxygen in a state of loose chemical combination with their red coloring matter, which is called **hæmoglobin**. Carbon monoxide combines with the hæmoglobin, forming a cherry-red compound which is much more stable than is the compound of hæmoglobin with oxygen. Consequently the red corpuscles become incapable of supplying oxygen to the body. Hence, poisoning by carbon monoxide is *suffocation*, though the blood is not blue, as in ordinary suffocation, but bright red, almost like arterial blood. Carbon monoxide is not poisonous to insects because their blood contains no red coloring matter.

The gas masks used in warfare provide efficient protection against many poisonous gases, but they are *useless against carbon monoxide*; they should never be employed, therefore, in mines or in other places in which the presence of this dangerous gas is suspected.

280. The burning of coal. The formation of carbon monoxide in a heater or stove will be understood from the diagram in Figure 145. In the bottom of the fuel bed the hot carbon meets abundant oxygen from the air and burns to carbon

dioxide. This, as it passes upward, finds itself in contact with glowing carbon in a region where no oxygen is available, and the carbon dioxide passes into carbon monoxide. At the top of the fuel bed the carbon monoxide meets oxygen admitted through the openings in the upper door and burns, with the well-known blue flame, to carbon dioxide.

In large plants, where the fuel bill may be thousands of dollars each week, the chimney gases are analyzed regularly. They should contain at least 10 per cent, and better 15 per cent, of carbon dioxide. No carbon monoxide should be present.

281. Producer gas. Carbon monoxide is a gaseous fuel of great industrial importance, being an important constituent of *producer gas*, *water gas*, and *coal gas*.

A gas producer (Fig. 146) produces carbon monoxide in the same way as does an ordinary stove. A regulated volume of air is forced into the bottom of the fuel bed, and since there is no upper door, the carbon monoxide meets no oxygen and does not burn. It passes out through the large pipe at the top, to be stored in gas holders or used.

Producer gas contains nearly one-third of its volume of carbon monoxide, the balance being chiefly nitrogen from the air of the blast. It burns with a blue flame. It is largely used in the industries as a fuel gas and as a gas-engine fuel.

282. Water gas. Water gas, which has about double the heating value of producer gas, is made by forcing steam upward through a white-hot fuel bed of coke or anthracite coal:

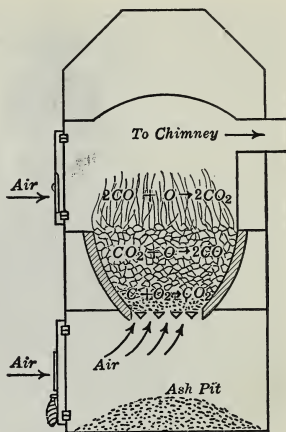
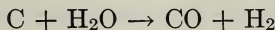
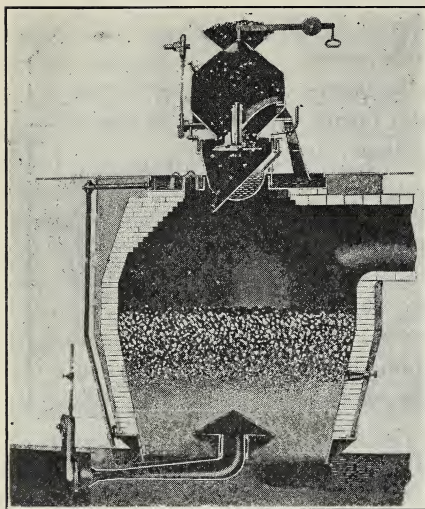


Fig. 145. Combustion in a coal fire.

Water gas consists chiefly of carbon monoxide and hydrogen, but it also contains a little carbon dioxide and nitrogen. In

addition it is "enriched" by being mixed with gaseous compounds of carbon and hydrogen derived from heated petroleum, which cause the finished water gas to burn with a luminous flame and increase its heat value.

Figure 147 is a diagram of the manufacture of water gas. During the "blow," as it is called, air is forced up through the fuel bed in the generator. This, of course, gives producer gas, which is led away to the left into



Courtesy of the Morgan Construction Co.

Fig. 146. Section of a gas producer.

the carburetor and thence into the superheater, where it is burned by air admitted for the purpose, as shown in the figure. The carburetor and super-heater are filled with a checkerwork of fire-brick, which is heated in about 10 minutes to a bright cherry-red, while the fuel bed in the generator becomes white-hot. During the "blow" the oil spray at the top of the carburetor is shut off.

Now the air blast is stopped, and the actual preparation of water gas, called the "run," begins. Steam is forced through the fuel bed, and the oil spray in the carburetor is turned on. The current of water gas from the generator sweeps the oil vapors downward through the carburetor and upward through the red-hot fire brick of the superheater, where they are con-

verted into permanent gases. Then the enriched gas is washed with a spray of water in the "scrubber," after which it is ready for use. When the "run" has lasted 5 minutes, the fuel bed in the generator becomes too cold to give good results. Then the steam and the oil spray are turned off, the air blast is turned on, and another "blow" begins.

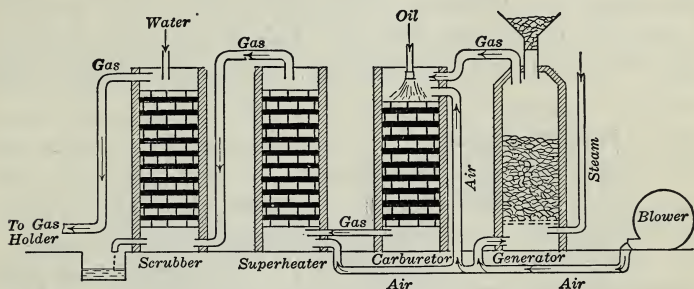


Fig. 147. Diagram of a water-gas plant.

283. Coal gas. Coal gas is made by distilling bituminous coal in vertical fire-clay retorts. The gas does not exist ready formed in the coal but is formed as the result of a highly complex chemical process which occurs when the coal is heated to redness in the absence of air. Thus, the making of gas from coal is not an ordinary distillation, like that of water, but resembles rather the heating of wood in closed vessels, for the coal and the wood do not distill as such but are destroyed and converted into other substances. **Destructive distillation**, as we have seen, is the term applied to processes of this kind.

The chief products of the destructive distillation of coal have been mentioned in connection with the manufacture of coke (§ 262). The coal tar produced is mainly composed of a large number of liquid and solid compounds of carbon and hydrogen. The ammonia that is formed must be carefully removed from the gas, for it would produce an unpleasant odor when the gas was burned. The same statement applies with

even greater force to another gaseous impurity, *hydrogen sulphide*, H_2S .

Figure 148 is a diagram of the manufacture of coal gas. The retorts are circular in cross-section and are wider at the bottom than at the top, so that the coke will fall out readily when the bottom is opened. They are filled and emptied by mechanical appliances. Eighteen of these retorts are often placed in 3 rows of 6 in the same furnace. This is heated by producer gas, which is burned outside of the retorts and in contact with

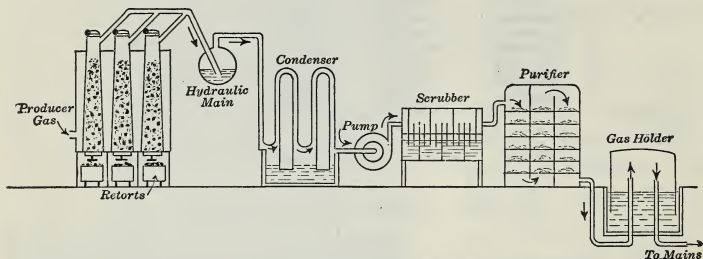


Fig. 148. Diagram of the manufacture of coal gas.

them. The producer gas is made in a separate furnace from the coke that is left in the retorts at the end of the operation.

Pipes lead the products of the distillation from the retorts to the *hydraulic main*, which is a long horizontal pipe in which some of the tar collects. The hydraulic main is so arranged as to remain half-filled with tar, under the surface of which dip the pipes from the retorts, so that the hot gas is forced to bubble through the tar.

The *condenser*, through which the gas next passes, is a series of long iron pipes kept cool by water circulating outside them. Here the gas is cooled and the tar removed except a small quantity which floats in the gas current in fine drops. This is taken out in the *tar extractor*, an appliance not shown in the diagram, in which the gas is made to pass repeatedly through perforated iron plates. This tar, along with that from the

hydraulic main and the condenser, flows into the *tar well*. The *exhauster*, the principle of which is similar to that of an electric fan, sucks the gas from the retorts through the hydraulic main, condenser, and tar extractor and pushes it through the *scrubber* and *purifier* into the *gas holder*.

The *scrubber* is a long horizontal cylinder half-filled with water, divided into compartments through which the gas passes in turn. In each compartment the water is agitated by numerous sheet-iron paddles, which rotate on a long horizontal shaft passing through the scrubber from end to end. These paddles keep the air filled with spray and, when they are above the water, expose numerous wet surfaces against which the gas streams, so that there is abundant opportunity for the ammonia to leave the gas and dissolve in the water.

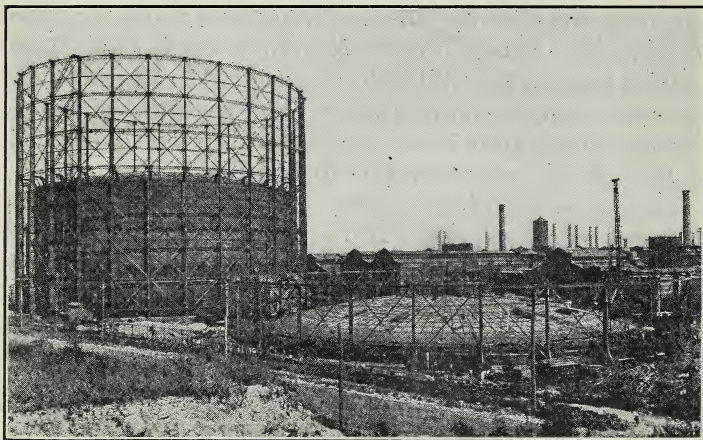
The necessity of freeing the gas from *hydrogen sulphide*, H_2S , has been mentioned. If this were allowed to remain, the gas flames of the household would give off the odor of burning sulphur, and their combustion products would discolor metal objects and bleach many colored fabrics. Another dangerous impurity in the crude gas is *hydrocyanic acid*, HCN , commonly called "*prussic acid*," which, because of its intense poisonous action, must be completely extracted.

To remove these two objectionable substances is the function of the *purifier*, a large cylindrical iron box containing perforated shelves, on which are spread layers of wood shavings covered with a special kind of iron ore composed of iron hydroxide, through which the gas slowly filters. Because of the necessity of removing the hydrogen sulphide and hydrocyanic acid as completely as possible, the gas is usually passed through 3 purifiers in series.

The purified gas is then measured in an enormous meter, and it is finally stored over water in the *gas holder*, which works on exactly the same principle as the bottles in which gases are collected in the laboratory. The gas holder is a great cylindrical box built of steel plates, the open end of which dips into

water. It is constructed in sections which slide out like the tubes of a telescope as the gas holder is filled. A gas holder of the largest size may have a capacity of 15,000,000 cu. ft. From the gas holder the gas is distributed to the consumers through mains which in large cities have a diameter up to 6 ft.

The gas supplied at present to eastern American cities is a mixture containing four-fifths of its volume of carburetted



Courtesy of the Consolidated Gas Co.

Fig. 149. Twin gas holders at Astoria, Long Island, the largest in the world, each with a capacity of 15,000,000 cu. ft.

water gas and one-fifth of its volume of coal gas. In the eastern United States, where anthracite coal and coke are abundant, water gas can be made more cheaply than coal gas, but pure water gas would be too dangerous for common use, for it has only a faint odor, and it contains nearly half its volume of carbon monoxide. The addition of the coal gas gives the unburned gas a smell that makes it easier to detect a leak, and the coal gas adds somewhat to the heat value. In the cities of the Far West illuminating gas is made from petroleum. The petroleum is vaporized by heat and the vapors led through

checkerworks of red-hot firebrick, which act like the super-heater of the water-gas process and convert the oil vapors into permanent gases.

In spite of the intense competition of electricity, the consumption of gas shows a steady gain from year to year. This is mainly due to the increasing use of gas for cooking, for which it has decisive advantages over solid and liquid fuels. On the other hand, *heating* with gas, though convenient, can hardly be commended from the standpoint of economy and sanitation. As a rule no provision is made for carrying off the combustion products of the gas radiator, and they escape into the room, charging the air with excessive quantities of carbon dioxide and water vapor and making it "stuffy" and unwholesome. Still more serious is the liability of the gas radiator to give off *carbon monoxide*, traces of which in the air cause headache, nervousness, and lowered vitality, while as little as 0.1 per cent is an immediate menace to life. In this respect radiators in which the flames are blue are more dangerous than those in which the luminous flame is employed. It may be added that the *exhaust of automobile engines* may give off dangerous quantities of carbon monoxide. Fatal accidents have occurred in small, ill-ventilated garages from this cause.

Since modern illuminating gas contains from one-quarter to one-third of its volume of carbon monoxide, leaks in the gas fixtures or pipes of a dwelling should receive prompt attention. The simplest way to look for leaks is to moisten the suspected place with soapy water. A flame fails to detect small leaks and is dangerous with large ones.

FLAME

284. Hydrogen when it unites with the oxygen of the air produces a **flame**, for the large amount of heat generated raises the temperature of the gas until it becomes luminous. Sulphur, though a solid, burns like hydrogen, with a flame, for

the sulphur is converted into vapor before it burns, and the vapor is raised by the heat of its own combustion to a temperature at which it radiates a blue light.

Iron, on the other hand, burns in oxygen with a brilliant light display but without flame. The reason for the difference is that the iron is *not vaporized* during its combustion, so that the chemical combination takes place entirely at the surface of the iron. The metal glows brightly but does not send forth any incandescent vapor to produce a flame.

Thus, the combustion of a gas or vapor, or of a solid or liquid that passes into a gas or vapor before burning, produces a flame, whereas the combustion of a solid that is not vaporized is flameless.

The **simplest possible flame** is that of burning hydrogen (Fig. 150). The interior is a dark cone of unburned hydrogen, to which oxygen does not penetrate. This is surrounded by a faintly luminous sheath of burning gas, outside of which the water vapor produced in the flame mingles with the air. The interior cone is cool, as can be shown by thrusting a match stick horizontally through the flame near the base, whereupon the wood will be charred in two places where it intersects the luminous sheath of the flame, but will not be affected in the center. The flame of burning carbon monoxide has the same simple structure.



Fig. 150.
Hydrogen
flame.

285. A candle flame is more complicated. Four different regions can be distinguished in it (Fig. 151). The cone immediately surrounding the wick appears dark by comparison with the second cone, which is just outside it and which radiates practically all the light yielded by the candle. Surrounding this in turn is a faintly luminous blue sheath, which can best be seen by looking through the flame at a dark surface held just behind it. Finally, there is a cup-shaped blue portion, which forms the

base of the flame and which extends upward until it meets the luminous cone.

The candle is made of a mixture of two white solids, *paraffin* and *stearic acid*, which consist chiefly of carbon and hydrogen. When the candle burns, this mixture is melted, drawn up by the wick, and vaporized, and the combustible gases thus formed make up the dark interior cone. This can be proved by lowering a piece of wire gauze upon the flame (Fig. 152). The gauze arrests the flame, but the combustible gases in the interior cone rise through it and can be ignited above the gauze by a match. Or, if the lower end of a piece of glass tubing be held in the inside of the flame, the combustible gases will pass through the tube and escape from its upper end, where they can be burned.



Fig. 151.
Candle
flame.

This combustible gas in the dark cone consists of various compounds of carbon and hydrogen. As they rise into the hotter portion of the flame, these compounds

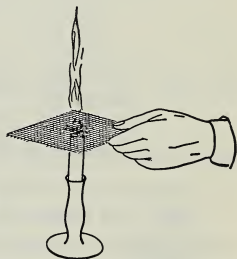


Fig. 152. Combustible
gases burning above
wire gauze.

are decomposed into hydrogen and carbon, and the latter takes the form of incandescent *lampblack*. The luminous cone owes its existence to these glowing particles of carbon, from which almost all the light of the flame proceeds. Their existence can be proved by holding in the flame a porcelain plate, which at once becomes coated with soot.

The outer blue mantle is the region of complete combustion, where the carbon and hydrogen are burned to carbon dioxide and water on coming into contact with unlimited oxygen from the air. The blue cup at the bottom is a second region of complete combustion due to the upward draft, which provides an

abundant supply of oxygen at the base of the flame, close to the wick.

So long as the wick is in the center of the flame, it cannot burn away, because of the lack of oxygen. As candles were formerly made, the charred portion of the wick had to be cut off from time to time, when it began to project into the luminous cone and enfeeble the light. This operation was called "snuffing" the candle. At present one thread of the braided wick is made shorter than the others, so that when released by the melting of the candle, the wick bends downward, and its glowing

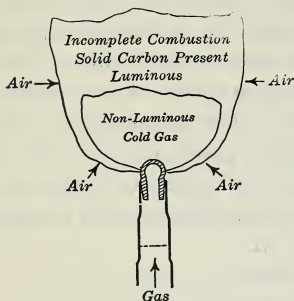


Fig. 153. The fishtail flame of the gas jet.

end projects out of the flame and is consumed by the oxygen of the air.

286. The flame of illuminating gas is identical in structure with the candle flame, possessing the same four regions, although the shape of the two flames is very different. The gas flame is purposely made as broad and thin as possible ("fish-tail" or "bat's-wing" flame) to increase the radiating surface. This is easily managed by so designing the burner as to allow the gas to escape through a slit of the proper size and shape. In the gas flame, as in that of the candle, the light comes entirely from glowing particles of carbon, which finally burn to carbon dioxide in the outer region by the oxygen of the surrounding air.

In the **Bunsen flame** incandescent particles of carbon cannot exist, for the gas is mixed with air before it is burned, and

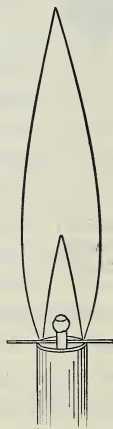


Fig. 154. A match unignited in the middle of a Bunsen flame.

oxygen for complete combustion is available in all parts of the flame. The inner cone is composed of the mixture of gas and air streaming out of the chimney of the burner. That the inner cone is cool compared with the rest of the flame can be shown by supporting a match in it, as indicated in Figure 154.

287. The safety lamp. Flame will not pass through wire-gauze because the metal conducts away the heat and cools the

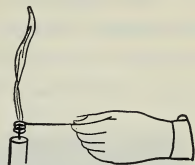


Fig. 155. Extinguishing a candle with a copper helix.



Fig. 156. Quenching burning alcohol by pouring through wire gauze.

combustible gas below its kindling point. This cooling effect can be shown by lowering a coil of copper wire upon a candle flame, which will be extinguished (Fig. 155). Burning alcohol can be quenched by pouring it through wire gauze (Fig. 156), the flame remaining above the gauze while the liquid passes through. *This experiment should not be repeated by the student, as a slight error in manipulation might lead to a serious burn.*

This behavior of wire gauze toward flame explains the constant use of wire gauze in the laboratory; it prevents the flame from coming into contact with glass vessels, which would lead to breakage. If a piece of wire gauze having about 20 meshes to the linear inch is held horizontal and brought down upon a lighted burner, the flame will spread out below the gauze but will not pass through unless the gauze is allowed to become red hot.

Or, if the gauze is held 2 inches above the burner, which is then turned on, and the gas lighted above the gauze, the

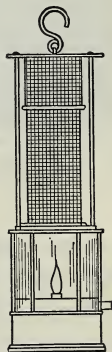
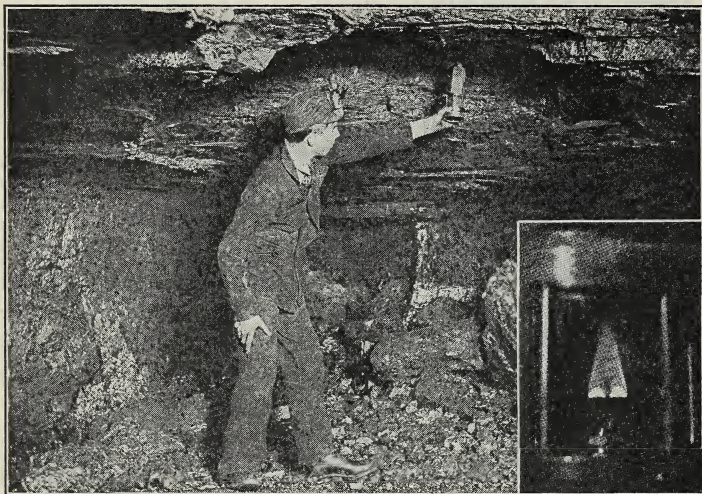


Fig. 157. The miner's safety lamp.

flame will continue to burn at the upper surface of the gauze without passing down to the burner.

The miner's *safety lamp* (Fig. 157), invented by Sir Humphry Davy in 1815, is an oil lamp in which the flame obtains its air supply through a cylinder of fine iron wire gauze (28 meshes to the linear inch) which is made double



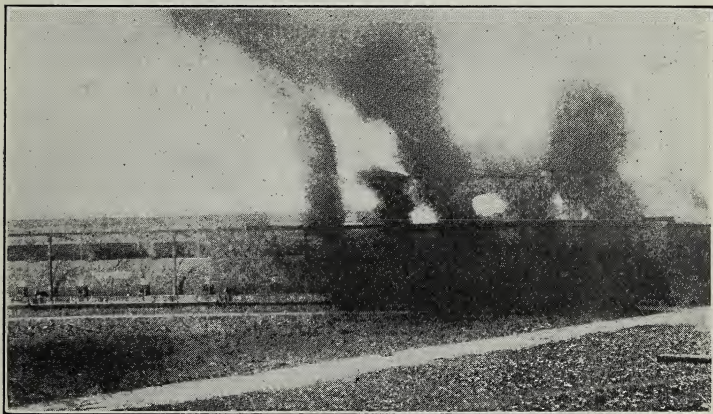
Courtesy of the Philadelphia Commercial Museum.

Fig. 158. Miner testing for fire damp with the safety lamp. Inset: the characteristic blue flame cap of methane.

at the top (the part most likely to become overheated) while the base is made of glass so as to give more light. A flame so protected cannot cause an explosion by setting fire to combustible gases outside the cylinder. The gases can pass *into* the cylinder and burn around the flame of the lamp, producing a blue cap on the flame which warns the miner of danger. This cap is noticeable when the air of the mine contains as little as 2 per cent of combustible gas by volume. Electric torches operated by dry cells are

also used in coal mines and are quite safe if properly constructed.

It must be remembered, of course, that explosions can be brought about, not only by the flame of the miner's lamp, but also by the blasting which is necessary to bring down the coal. *Coal dust* suspended in the air of a mine is highly dangerous and has caused many fatal explosions. This is especially true in winter, when the mines are dry and the dust rises more easily.



Courtesy of the Bureau of Mines.

Fig. 159. Experimental explosion of coal dust in the testing gallery of the United States Bureau of Mines.

288. The gas mantle. Gas as an illuminant would be unable to compete with the electric light were it not for the invention of the *gas mantle*, which furnishes light at about one-fifth the cost of that supplied by the luminous gas flame. In mantle lighting the gas is mixed with air before combustion, so as to produce a Bunsen flame. In this flame is supported a gauzy, infusible mantle, which becomes heated to incandescence and is the sole source of light. In modern gas lamps the Bunsen flame is *inverted*, so that the light from the mantle is thrown

downward where it is needed, instead of being dissipated outward and upward as with the upright mantle.

The first step in the mantle manufacture is the weaving of the mantle fabric. Cheaper mantles are woven of long-fibre cotton. Inverted mantles are made of the stem fibre of *ramie*,

often called *China grass*, which is a variety of nettle growing in China and other parts of the Far East. Especially high-grade mantles are woven of artificial silk, which gives exceptional strength, candle power, and freedom from shrinkage.

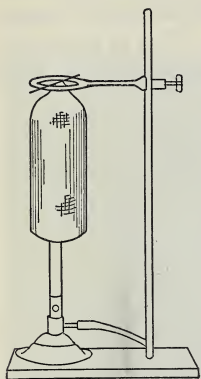


Fig. 160. Principle of the Welsbach lamp.

The next process is to dip the mantle into a colorless liquid called the "lighting fluid," which is a water solution of the nitrates of two rare elements, *thorium* and *cerium*. The lighting fluid contains about 99 times as much thorium as it does cerium. Any departure from these proportions in the lighting fluid impairs the light-giving power of the finished mantle, more thorium

giving a feeble bluish-white light, and too much cerium a dull yellow.

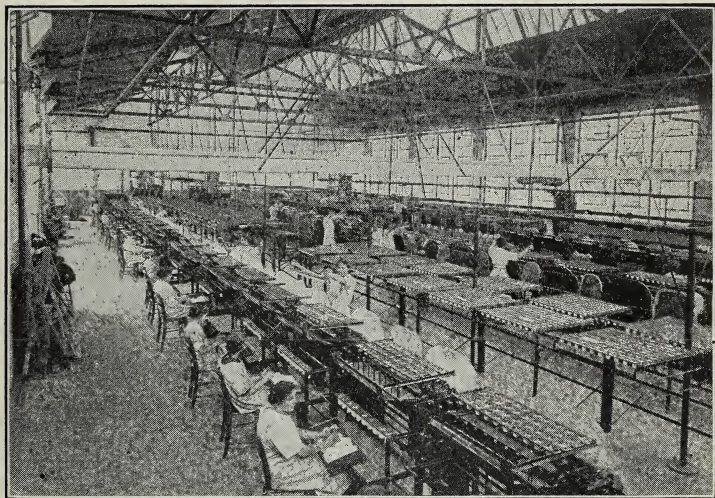
After treatment with the lighting fluid the mantle is dried and burned, which destroys the vegetable fibre and at the same time converts the nitrates of thorium and cerium into a residue of the oxides of those elements which retains the shape of the woven fabric. This is then heated to a high temperature with a blowpipe flame, which hardens it and smooths out wrinkles and inequalities, producing a better shape.

This ends the actual process of manufacture of the mantle, which at this stage is a white, gauzy structure consisting of 98.75 per cent of thorium oxide (ThO_2) and 1.25 per cent of cerium oxide (CeO_2). In this condition the mantle is too fragile for transportation, and consequently it is now dipped into an alcoholic solution of *collodion* and dried. The collodion makes

the mantle strong enough to be packed and shipped and burns off at once when it is placed in use.

OTHER CARBON COMPOUNDS

289. Methane, CH_4 . The compounds of carbon and hydrogen are called **hydrocarbons**, and 200 or more of them are known. The simplest of all compounds of carbon and hydrogen



Courtesy of the Welsbach Co.

Fig. 161. Hardening furnaces for inverted gas mantles.

finds a place at this stage of our work; some more complex hydrocarbons of great industrial importance will be discussed in a later chapter.

Methane, CH_4 , often called **marsh gas**, is formed when vegetable matter decays under water and is liberated in impure condition when the muck at the bottom of a stagnant pool is stirred with a stick. The bubbles can be ignited with a match at the surface, or the gas can be collected as shown in Figure 162.

Methane is the chief constituent of **natural gas**, which is obtained in enormous volumes from wells drilled for the purpose in Pennsylvania, Ohio, West Virginia, Illinois, Kansas, and other states. Natural gas is an excellent fuel. Its heat value is nearly 1,200 British thermal units per cubic foot, which

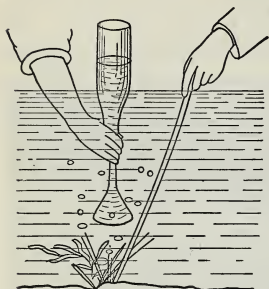
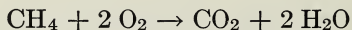


Fig. 162. Collecting methane.

is about twice the corresponding figure for illuminating gas, and it is much cheaper. The flame of natural gas is not luminous, but it gives an excellent light when burned with a mantle. It is largely employed as a domestic and industrial fuel and for the manufacture of carbon black.

Methane is called "**fire damp**" by the coal miner, from an old word "**damp**," which means a gas or vapor. Methane exists under pressure in cavities in the coal. When they are tapped it escapes, often with a hissing noise. Fresh coal from some mines is so saturated with gas that bubbles rise from it when it is dropped into water.

Methane is odorless, so that the sense of smell gives no warning of its presence in the air of a mine. It is only about half as dense as air, and like all light gases it rapidly diffuses through air, with which it forms an explosive mixture when only one-fourteenth by volume of methane is present:



Thus the oxygen of the mine air is removed by the explosion, and those who have escaped it are exposed to the danger of being suffocated by the carbon dioxide produced, which is called "**after damp**" by the miners.

In the laboratory methane is prepared by heating *sodium acetate*, $\text{NaC}_2\text{H}_3\text{O}_2$, with a mixture of sodium hydroxide

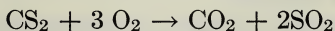
and lime. The lime does not enter into the chemical change:



Methane is a colorless, odorless gas, which dissolves only slightly in water. Its molecular weight, as shown by the formula CH_4 , is 16. Hence its specific gravity referred to air is $\frac{16}{29}$, or 0.55. Methane has been liquefied and solidified by great pressure and cold. Liquid methane is one of the lightest liquids known, being only two-fifths as dense as water.

Methane is combustible, burning with a blue flame, according to the equation already given, to carbon dioxide and water, and, like all combustible gases and vapors, it forms an explosive mixture with air. As already indicated in connection with natural gas, methane is of great importance as an industrial fuel. Coal gas contains about one-third of its volume of methane, and water gas a smaller proportion.

290. Carbon disulphide, CS_2 . Carbon disulphide is made by heating a mixture of charcoal and sulphur in a large electric furnace. It is a dense, colorless liquid, which refracts light strongly and is scarcely soluble in water. When pure it has rather a pleasant odor, but the commercial substance contains impurities which give it a disgusting smell. It vaporizes rapidly when exposed, and the vapor is poisonous. Carbon disulphide is highly inflammable, and in working with it in the laboratory great care should be taken to avoid danger of fire. When ignited it burns with a blue flame to a mixture of 1 volume of carbon dioxide and 2 volumes of sulphur dioxide:

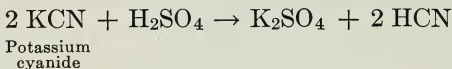


Carbon disulphide is used as an *insecticide*. When a little of it is sprinkled over wheat infected with weevils, the vapor of the carbon disulphide, which is 3 times as heavy as air, descends through the grain and, without injury to the wheat, destroys

the insects. Carbon disulphide can be used to kill parasites at the roots of plants and moles in their burrows, but care is required, as an excess of it is injurious to vegetation. Carbon disulphide is largely employed as a solvent for oils, fats, and waxes, and for vulcanizing rubber.

291. Cyanogen, C_2N_2 . Cyanogen is a colorless gas which smells like bitter almonds, burns with a pink flame, and is intensely poisonous.

292. Hydrocyanic acid, HCN. Hydrocyanic acid is the dangerous poison commonly called "**prussic acid.**" It can be obtained by treating potassium cyanide with sulphuric acid:



Pure hydrocyanic acid is a colorless liquid, lighter than water, which smells like bitter almonds. It evaporates so rapidly that when a little of it is exposed in a watch glass, it is frozen by the cold produced by its own evaporation. It is highly poisonous, and even a small quantity taken internally causes death almost instantaneously. The same result follows the inhalation of the vapor unless it is very much diluted with air. A very dilute solution of hydrocyanic acid (2 per cent) is employed in medicine as a heart stimulant.

SUMMARY

The *atoms* of carbon have a power of forming **chain-like unions** with each other. For this reason the compounds of carbon are very numerous.

Carbon dioxide is prepared in the laboratory by the action of hydrochloric acid on cracked marble:

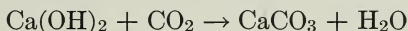


Liquid carbon dioxide, sold commercially in strong steel cylinders, is used for "carbonating" beverages.

Small percentages of carbon dioxide in air have little effect on the body; 4 per cent causes marked discomfort, and 10 per cent is dangerous.

Carbon dioxide when dissolved in water combines with it to form carbonic acid, H_2CO_3 , which gives the water a refreshing taste. **Soda water** is made by forcing carbon dioxide into solution in water under pressure.

Lime water, which is a dilute solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$, is rendered milky by carbon dioxide, owing to the formation of a precipitate of *calcium carbonate*, CaCO_3 :



Carbon monoxide, CO , is formed by the action of carbon dioxide upon glowing carbon: $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$.

Carbon monoxide burns in air to carbon dioxide. It removes the oxygen from many oxides of the metals, and this property is extensively utilized in extracting iron from its ores. It is intensely poisonous.

Producer gas is made by burning coal or coke with a regulated air blast so that the oxygen supply is only sufficient to form carbon monoxide. Its chief constituents are carbon monoxide and nitrogen.

Water gas is obtained by blowing steam through a white-hot fuel bed of coal or coke. It is composed chiefly of carbon monoxide and hydrogen.

Coal gas is made by heating soft coal in the absence of air. It contains hydrogen and carbon monoxide along with methane and other hydrocarbons.

A **flame** is produced by a burning gas or vapor. A *solid* will yield a flame only if vaporized by the heat of its own combustion.

The **light** radiated from ordinary flames proceeds from glowing solid particles of carbon, which are formed by the decomposition of the hydrocarbons undergoing combustion.

The **gas mantle** is a gauzy infusible structure containing 98.75 per cent of *thorium oxide*, ThO_2 , and 1.25 per cent of *cerium oxide*, CeO_2 .

Methane, CH_4 , is the simplest hydrocarbon. Natural gas, marsh gas, and fire damp are chiefly methane.

Carbon disulphide, CS_2 , is made by heating charcoal and sulphur in an electric furnace.

EXERCISES

1. What is the reason for the large number of compounds of carbon?

2. What is the main difference in composition between free air and the air in the soil?

3. Would it be suicidal or merely very dangerous to descend into a well in which a lighted candle was extinguished?

4. Explain the effervescence of soda water.

5. What is the difference between *carbon dioxide* and *carbonic acid*? Criticize the statement that the air contains 0.04 per cent of carbonic acid.

6. Discuss the part played in the nutrition of plants (a) by carbon dioxide, (b) by carbonic acid.

7. What is the cause of the blue flame that plays over the surface of a coal fire? Why do explosions often occur in stoves after coal is added?

8. What are some of the advantages of gaseous fuel over solid fuel?

9. Coal gas contains about 15 per cent by volume of carbon monoxide. Is it more or less poisonous than water gas?

10. Explain the connection between flame and the *volatility* of the burning substance.

11. Why was it necessary to "snuff" a burning candle? How has snuffing been made unnecessary?

12. What is *destructive distillation*? Name some products of the destructive distillation of wood. Of coal.

13. Give two methods of distinguishing between carbon monoxide and carbon dioxide.

14. How could you prove that methane contains carbon?

15. How many liters of carbon dioxide at 0° and 760 mm. are produced when 25 grams of marble dissolve in hydrochloric acid?
16. What is the volume (*a*) of 50 grams of carbon monoxide, (*b*) of 50 grams of carbon dioxide?
17. How many liters of carbon dioxide must be passed through glowing charcoal to yield 42 grams of carbon monoxide?
18. What volume of carbon dioxide is formed by the burning of 30 liters of carbon monoxide, and what volume of oxygen is required? Solve by inspection.
19. How many grams of carbon are there (*a*) in 2.8 liters of carbon dioxide, (*b*) in 2.8 liters of carbon monoxide?
20. How many liters of carbon dioxide would be formed by burning a diamond weighing 15 carats in oxygen (1 carat = 0.2 gram)?
21. How many grams of sodium acetate are needed to make 8 liters of methane?

REVIEW QUESTIONS

1. Why do combustibles burn more rapidly in compressed air than in ordinary air?
2. Nitric acid acts at the same time as an acid and as an oxidizing agent. Explain this statement.

CHAPTER XXVII

SULPHUR (S=32) AND ITS SIMPLER COMPOUNDS

293. Occurrence. Sulphur occurs native in extensive beds in Louisiana, Texas, Sicily, and Japan. The Louisiana deposit is especially noteworthy. Beginning about 700 ft. below the earth's surface, it is a great, circular mass of pure sulphur 500 ft. thick and half a mile wide. On a small island in the Pacific just north of Japan are three volcanic peaks nearly 3,000 ft. high which are largely composed of sulphur. It is estimated that in this locality 1,500,000 tons of sulphur are exposed on the surface. Large quantities of sulphur have been obtained from the Sicilian mines, but here it occurs mixed with gypsum and requires purification before it is fit for export.

Sulphur compounds are abundant in nature. The compounds of sulphur with the metals are called **sulphides**, and some of them, like *lead sulphide*, PbS , and *zinc sulphide*, ZnS , are important ores. The **sulphates** are the salts of *sulphuric acid*, H_2SO_4 . *Calcium sulphate*, CaSO_4 , is the mineral **gypsum**, and *barium sulphate*, BaSO_4 , is commonly called **barytes**. These and other sulphates occur abundantly in nature and are minerals of great economic importance.

In chemical combination sulphur is found in all animals and plants. Such materials as horns, hoofs, muscular tissue, and nerve fibres always contain it. Among plants rich in sulphur are onions, garlic, mustard, radishes, turnips, cabbages, and alfalfa. A sufficient supply of sulphur compounds in the soil is essential to the growth of plants, especially of those just mentioned.

294. Extraction of sulphur. The Louisiana sulphur deposit lies under a quicksand through which it is next to impossible

to sink a shaft. Moreover, large quantities of the highly poisonous gas *hydrogen sulphide*, H_2S , escape from the sulphur bed and saturate the neighboring rocks. For these reasons the sulphur cannot be mined by the ordinary methods. It is extracted by the very ingenious *Frasch process*. Three concentric steel pipes are driven through the overlying strata into the deposit, the inner pipe having a diameter of 1 in., the middle pipe of 3 in., and the outer pipe of 6 in. (Figure 163). Superheated water is driven down through the space between *A* and *B* and escapes through *CC* into the deposit, melting the sulphur. The liquid sulphur finds its way through *EE* into the chamber *D*, whence it is lifted to the surface between *B* and *F* by compressed air, which is forced down through the inner pipe *F*.

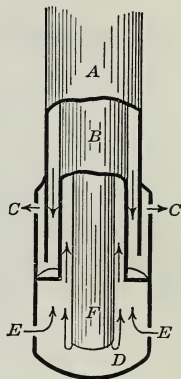


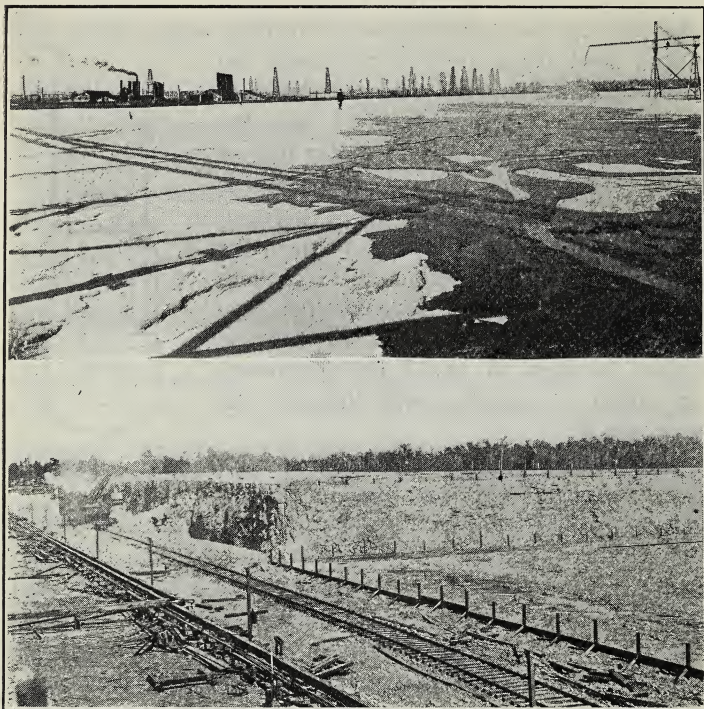
Fig. 163. Diagram of the Frasch apparatus.

The melted sulphur is allowed to run into a huge bin 50 ft. high, built of planks, where it solidifies to form a block which may contain 100,000 tons. This is broken up by blasting and shipped. The sulphur is so pure that for most purposes no refining is needed. Sulphur is also extracted at Freeport, Texas, in the same way. The United States not only produces all the sulphur consumed at home, but also exports sulphur to Europe.

In Sicily the lumps of sulphur ore are piled in large heaps in shallow pits lined with plaster. These are covered with powdered burnt residue from a previous heap. Air canals are left in the interior of the pile, so that the air has a limited access. Then the sulphur is ignited. A smothered combustion lasting some weeks ensues, during which one-third of the sulphur is burned; the balance is melted by the heat and flows out.

The crude sulphur obtained in this way is exported. It

still contains 3 per cent of impurities, consisting of calcium sulphate, arsenic, and other substances. It is refined by distillation from cast-iron retorts, the sulphur vapor from the



Courtesy of the Union Sulphur Co.

Fig. 164. Sulphur extraction by the Frasch process: above, discharge of melted sulphur; below, loading solid sulphur with a steam shovel.

retort being led into a small brick chamber on the floor of which melted sulphur collects. From time to time the liquid is withdrawn and poured into circular moulds of wood, in which it solidifies to form the familiar brittle yellow cylinders that are known in commerce as **roll sulphur**.

Flowers of sulphur is obtained by leading the sulphur vapor from the retort into a large brick chamber the walls of which remain cold. The sudden cooling condenses the vapor to a fine yellow powder, which is at first amorphous but which becomes crystalline on being preserved.

295. Physical properties.

Sulphur is a brittle, yellow solid twice as dense as water. It is a non-conductor of electricity and a very bad conductor of heat. It melts at 115° to a thin, light-yellow liquid. When this liquid is heated to 200° , it forms a dark jelly-like mass, so thick that the flask containing it can be inverted without the contents running down the sides.

Heated to a still higher temperature, the jelly again forms a thin liquid, but it is now reddish-black and nearly opaque. At 444° the sulphur boils. The vapor is at first yellow, but its color gradually deepens with rising temperature until at a faint red heat it is blood-red. This variation in color would lead us to suspect that some change in the sulphur molecule occurs on heating. As a matter of fact, the density of sulphur vapor shows that the molecule is at low temperatures S_8 and at high temperatures S_2 .

Sulphur, though insoluble in water, is freely soluble in carbon disulphide, in sulphur chloride, S_2Cl_2 , and in warm turpentine, and it has been shown that the molecule of dissolved sulphur contains 8 atoms.

296. Chemical conduct. Sulphur oxidizes slowly in the air at ordinary temperatures. It ignites at $260^{\circ}C.$, burning with a blue flame and giving off a suffocating smell. The odor of burning sulphur is due to the colorless gas *sulphur dioxide*,

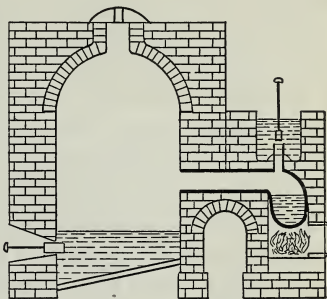


Fig. 165. Sulphur distilling furnace.

SO₂, which is the main product of the combustion, though some *sulphur trioxide*, SO₃, is also formed.

When heated, sulphur combines directly with many of the elements, both metals and non-metals. A mixture of powdered iron with flowers of sulphur becomes incandescent when heated gently and passes into a black mass of *ferrous sulphide*, FeS. A mixture of zinc dust with half its weight of flowers of sulphur, when ignited with a match, burns like gunpowder, producing a dense white smoke of *zinc sulphide*, ZnS. Potassium and sodium burn in sulphur vapor. A spiral of copper wire glows brightly when introduced into sulphur vapor and passes into a brittle black mass of *copper sulphide*, Cu₂S.

It will be seen from these facts that sulphur is one of the *active* non-metals. Although there are many exceptions to the rule, it is useful to remember that the *most frequent valence* of sulphur is 2. Since oxygen is also bivalent, the compounds of sulphur and of oxygen with the same element often correspond in their formulas:

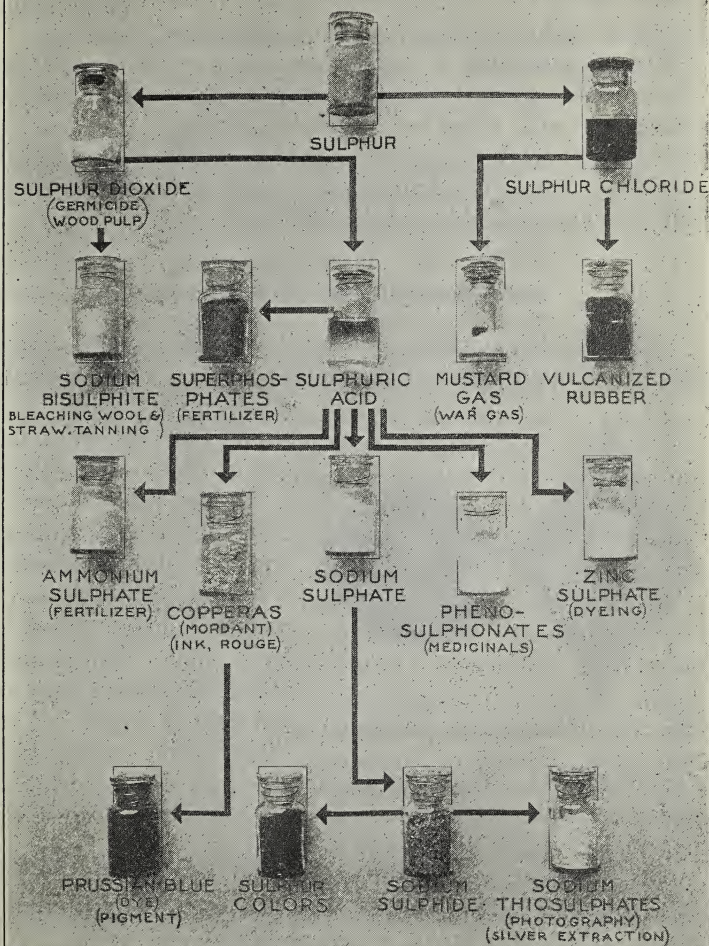
Oxygen Compounds		Sulphur Compounds	
Water	H ₂ O	Hydrogen sulphide.....	H ₂ S
Carbon dioxide.....	CO ₂	Carbon disulphide.....	CS ₂
Mercuric oxide.....	HgO	Mercuric sulphide.....	HgS
Zinc oxide.....	ZnO	Zinc sulphide	ZnS
Lead oxide	PbO	Lead sulphide.....	PbS

297. Uses of sulphur. Sulphur is used in the manufacture of sulphuric acid, black gunpowder, and carbon disulphide, of the two important pigments ultramarine and vermilion, and in vulcanizing rubber. Another large use of sulphur is in *bleaching wool*, which is done by hanging the yarn or fabric in a closed chamber in which sulphur ($\frac{1}{12}$ of the weight of the wool) is burned to sulphur dioxide. Silk is often bleached in the same way.

In Philadelphia melted sulphur is employed as a cement in setting up the posts supporting trolley wires. It is excellent for this purpose, being waterproof and one of the best of insu-

SULPHUR PRODUCTS

IN WAR AND PEACE TIME INDUSTRIES



Courtesy of the National Research Council.

Fig. 166. Principal products derived from sulphur.

lators. Flowers of sulphur is used in medicine in the treatment of sore throat and kindred troubles. Finely powdered sulphur strewn upon the leaves is successfully used as a remedy for various diseases of the grapevine caused by microscopic mildews and moulds which have at times devastated vineyards.

Notable quantities of sulphur are consumed in making the "lime-sulphur spray," which is a clear, yellow liquid made by boiling lime with water and powdered sulphur. It should be made in the open air, as the vapors from the boiling liquid attack the eyes. The lime-sulphur spray is largely used on fruit trees as a fungicide and insecticide.

ALLOTROPIC FORMS OF SULPHUR

298. Rhombic sulphur. Beautiful crystals of pure native sulphur are often found in the Sicilian mines. These crystals

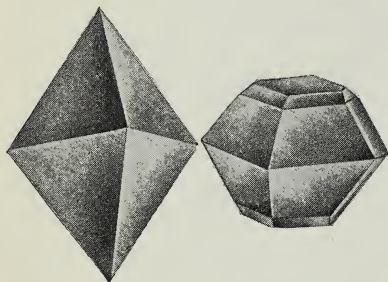


Fig. 167. Crystals of rhombic sulphur.

sometimes have the simple form shown at the left in Figure 167, which is like two rhombic pyramids placed base to base and is called a *rhombic octahedron*. More commonly sulphur crystals have more complicated forms like that shown at the right in Figure 167 or those of the natural crystals in Figure 34. These forms, however, are all related to the regular rhombic octahedron and can be derived from it by imagining its edges and angles to be cut off.

This allotropic form of sulphur is called, because of the form of the crystals, *rhombic sulphur*. It is the only form that occurs native. Rhombic sulphur is lemon-yellow and brittle. Its specific gravity is 2.06, and it melts at 115° .

Crystals like those shown in Figure 167 are easily obtained in the laboratory by dissolving powdered roll sulphur in carbon disulphide and allowing the solution to evaporate on a watch glass.

299. Prismatic sulphur. When melted sulphur is allowed to cool, it forms a mass composed of interlacing needle-like crystals, each of which is a long inclined prism, as shown in Figure 168.

This allotropic form, which is called **prismatic sulphur**, is pale yellowish-brown, and the crystals are flexible. The specific gravity is 1.96, and the melting-point 119° . Prismatic sulphur is *unstable*. When kept over night the crystals become lemon-yellow and brittle. Although the external prismatic shape is preserved, examination with the microscope shows that each prism has changed into a mass

of little crystals of rhombic sulphur. This transformation explains the fact that prismatic sulphur is not found in nature.



Fig. 168. Form of crystal of prismatic sulphur.

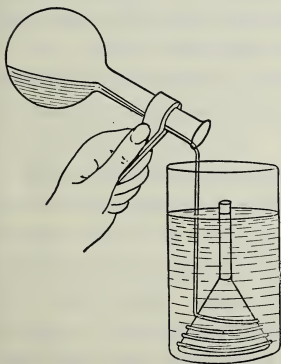


Fig. 169. Pouring soft sulphur.

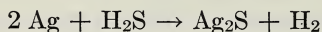
Roll sulphur when first made is composed of crystals of prismatic sulphur, but long before the sulphur is marketed, the rolls are completely changed to the rhombic modification.

300. Soft sulphur. Soft sulphur is made by pouring boiling sulphur in a thin stream into water (Fig. 169). The sudden cooling converts the sulphur into a transparent, yellowish-brown, stringy mass, which is elastic like rubber but less tenacious. Soft sulphur is unstable, becoming brittle when preserved. This is due

to the gradual change of the soft modification into a mass of small crystals of rhombic sulphur.

HYDROGEN SULPHIDE (H_2S)

301. Occurrence. Hydrogen sulphide is found in the gases that escape from volcanoes up to 25 per cent by volume. It occurs dissolved in the water of sulphur springs, where it can be detected by exposing to the gas bubbling up from the water a silver coin, which is turned black by the production of a film of silver sulphide upon its surface:



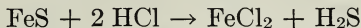
Eggs contain sulphur, especially in the white portion, and when they decompose, hydrogen sulphide is liberated. This is the cause of the odor of rotten eggs. A trace of hydrogen sulphide escapes when a boiled egg is opened, even though the egg be perfectly fresh, which explains the fact that silver spoons become tarnished when boiled eggs are eaten with them.

By the putrefaction of animal matter containing sulphur, hydrogen sulphide is formed in *sewers*, and it is often contained in dangerous quantities in sewer gas. Hydrogen sulphide is one cause of the evil odor of drains that are clogged and unclean.

Coal always contains sulphur. When a kettle boils over on a hot fire, a little of the hydrogen set free from the water unites with the sulphur of the coal, producing hydrogen sulphide, which can be detected by its odor. Since the air admitted below the grate contains abundant water vapor, traces of hydrogen sulphide are formed in all coal fires, and the odor of the gas is often noticeable in every room of a house heated by a badly constructed hot-air furnace. This is a most unwholesome condition. In addition to its bad effect on the body, hydrogen sulphide in the air of the household is destructive to potted plants. It rapidly tarnishes silverware and

slowly blackens oil paintings by converting the lead of the pigments into black *lead sulphide*, PbS.

302. Preparation. Hydrogen sulphide is made in the laboratory by the action of dilute hydrochloric acid on *iron sulphide*, FeS:



For making small quantities of hydrogen sulphide a test-tube generator is convenient (Fig. 170).

Many sulphides of the metals yield hydrogen sulphide when treated with hydrochloric acid. Iron sulphide, however, is in general use for the purpose because it is convenient and easily made. To prepare iron sulphide for generating hydrogen sulphide a mixture of iron filings with three-fifths of its weight of sulphur is heated to redness in a crucible. A hard, black, metallic mass results, which is broken up to an average diameter of about $\frac{1}{8}$ in. for use.

303. Physical properties.

Hydrogen sulphide is a colorless gas which is at once distinguished from all other gases by its disgusting odor of rotten eggs. Its specific gravity referred to air is 1.18 when determined by experiment. This is in agreement with the formula H_2S , from which the specific gravity referred to air ought to be $\frac{34}{29}$, or 1.18.

Hydrogen sulphide condenses at -62° to a transparent liquid, which freezes at -83° to an ice-like solid. A liter of water at room temperature dissolves 3 liters of hydrogen sul-

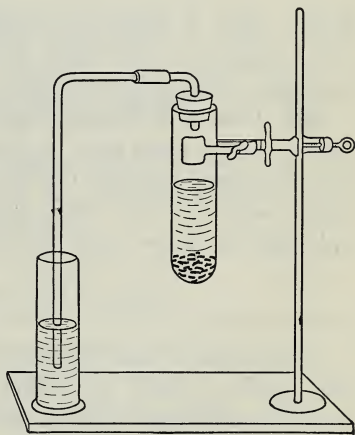
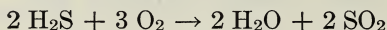


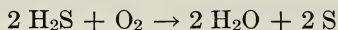
Fig. 170. Preparation of hydrogen sulphide.

phide, and the solution is much employed in the laboratory in testing for metals like lead, copper, etc., in water solutions of their compounds.

Chemical conduct. Hydrogen sulphide is combustible, burning with a blue flame to sulphur dioxide and water:

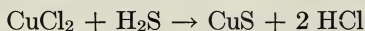


When the supply of air is limited, the hydrogen burns to water, but the sulphur separates in the free state:

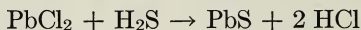


Hence, when a bottle of hydrogen sulphide is ignited with a match, there is a blue flame which is due to the burning of the hydrogen, while a film of sulphur deposits on the glass.

304. Uses of hydrogen sulphide. When hydrogen sulphide, issuing from a glass tube, is allowed to bubble through a solution of copper chloride, CuCl_2 , there is a black precipitate of *copper sulphide*, CuS , while hydrogen chloride is also formed and dissolves in the water present:



A solution of lead chloride, PbCl_2 , or of any other salt of lead, gives a black precipitate of *lead sulphide*, PbS , when hydrogen sulphide is passed through it:



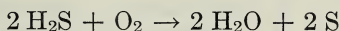
This test is so delicate that it will detect without difficulty one part of lead in a million parts of water.

A solution containing a soluble compound of *antimony* gives with hydrogen sulphide an orange precipitate of *antimony sulphide*, and in a solution in which *arsenic* is present hydrogen sulphide produces a yellow precipitate of *arsenic sulphide*.

These instances illustrate the use of hydrogen sulphide in testing solutions for compounds of the *heavy metals*. When hydrogen sulphide, under proper conditions, is passed into a solution containing a salt of a heavy metal, the sulphide of the metal is precipitated. These sulphides have characteristic colors or other properties that make it easy to identify the metal present with great certainty. Because of the disagreeable odor and poisonous action of hydrogen sulphide many attempts have been made to find a substitute for it, but it still remains a necessity in the chemical laboratory.

305. Action on the body. Hydrogen sulphide is *poisonous*. In working with it care should be taken to inhale as little as possible. The result of filling the lungs with it is almost instantaneous death. In smaller quantities it causes headache, nausea, and depressed vitality. The atmosphere in sewers often contains enough hydrogen sulphide to cause fatal accidents.

The poisonous action of hydrogen sulphide is due to the fact that it removes the oxygen from the hæmoglobin of the red blood corpuscles, forming water with it:



Hæmoglobin is a compound of iron, and the sulphur momentarily liberated in this process converts the iron of the red corpuscles into iron sulphide. Thus the corpuscles are poisoned and rendered incapable of carrying oxygen about the system.

306. The formula of hydrogen sulphide. Thus far we have taken the formula H_2S for granted. Let us now examine the evidence on which it is based.

The specific gravity of hydrogen sulphide referred to air is 1.18. Hence its molecular weight must be 1.18×29 , or 34. Now chemical analysis shows that hydrogen sulphide has the following composition:

Hydrogen.....	5.88 per cent
Sulphur.....	94.12 per cent

Hence, of the 34 parts by weight in a molecule, 34×0.0588 , or 2, parts must be *hydrogen*. Since the atomic weight of hydrogen is approximately 1, there are 2 atoms of hydrogen. Also 34×0.9412 , or 32, parts by weight of the hydrogen sulphide molecule must be *sulphur*. Since 32 is the atomic weight of sulphur, this corresponds to 1 atom of sulphur. Hence the formula of hydrogen sulphide is H_2S .

The same result is obtained by the experiment shown in Figure 171. The flask is filled with hydrogen sulphide. There is a little tin in the bottom. The U-tube contains mercury, which, to protect it against the hydrogen sulphide, is covered with a layer of oil in the limb next the flask.

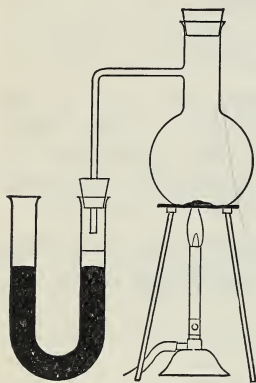


Fig. 171. Apparatus for determining the formula of hydrogen sulphide.

By the cautious application of a flame to the bottom of the flask, the tin is gently warmed. It combines with the sulphur, forming tin sulphide and liberating the hydrogen, which is found after cooling to occupy the same volume as the hydrogen sulphide.

Since equal volumes of gases contain equal numbers of molecules, this proves that each molecule of hydrogen sulphide has yielded a molecule of hydrogen. But the molecule of hydrogen contains 2 atoms. Hence the molecule of hydrogen sulphide contains 2 atoms of hydrogen.

We have seen that the molecular weight of hydrogen sulphide is 34. Since it contains nothing but hydrogen and sulphur, the weight of the sulphur in the molecule must be $34 - 2$, or 32. But 32 is the atomic weight of sulphur. Hence the molecule of hydrogen sulphide contains 2 atoms of hydrogen and 1 atom of sulphur, and the formula of the gas is H_2S .

OTHER SULPHUR COMPOUNDS

307. The sulphides of the metals. The sulphides of the metals are minerals of great economic value as ores of the metals. They are dense, crystalline solids which have a metallic luster but are not malleable. They will be studied under the corresponding metals. Some of the more important are enumerated in the following table:

IMPORTANT MINERAL SULPHIDES

	Lead	Mercury	Zinc	Iron
CHEMICAL NAME.	Lead sulphide	Mercuric sulphide	Zinc sulphide	Iron disulphide
COMMON NAME...	Galena	Cinnabar	Zinc blende or Sphalerite	Pyrite
FORMULA	PbS	HgS	ZnS	FeS ₂
COLOR	Lead-gray	Red	Brown to black	Brass-yellow
USE	Chief ore of lead	Chief ore of mercury	Chief ore of zinc	Manufacture of sulphuric acid
CORRESPONDING OXIDE	PbO	HgO	ZnO	None

308. Sulphur chloride, S₂Cl₂. Sulphur chloride is made by passing chlorine over boiling sulphur, whereupon sulphur chloride is formed as a vapor, which is condensed by cooling. It is a light-yellow liquid with an offensive odor, and its vapor is poisonous when inhaled. Sulphur chloride is an excellent solvent for sulphur, and it is used in vulcanizing rubber.

The simple formula SCl represents the same percentage composition as S₂Cl₂, and the question arises why the doubled formula is used. The answer is that the specific gravity referred to air of the vapor of sulphur chloride is 4.66. Multiplying this by 29, we find that its molecular weight must be 135. But the formula SCl corresponds to a molecular weight

of only 67.5, which is one-half of 135. Hence the molecule of sulphur chloride possesses the *doubled formula* S_2Cl_2 and contains 2 atoms of sulphur and 2 of chlorine.

SUMMARY

Inexhaustible deposits of **native sulphur** exist in *Louisiana* and *Texas*, and large quantities are also obtained in *Sicily*. Some of the **sulphides** and **sulphates** of the metals are minerals of great economic value. Sulphur compounds are found in all fertile soils and in all animals and plants.

Sulphur burns with a blue flame in air or oxygen to **sulphur dioxide**, SO_2 , which is a suffocating gas. Many of the metals burn in sulphur vapor, forming sulphides.

Sulphur is often **bivalent**, and since the same is true of oxygen, the oxides and sulphides of the same element often correspond in their formulas.

Sulphur exists in a number of **allotropic forms**, of which *rhombic sulphur*, *prismatic sulphur*, and *soft sulphur* are the most important.

Sulphur is employed in the manufacture of sulphuric acid and black gunpowder, in bleaching wool, in vulcanizing rubber, and in making sprays for fruit trees.

Hydrogen sulphide, H_2S , is a colorless, foul-smelling, poisonous gas, which is obtained by the interaction of iron sulphide, FeS , with hydrochloric acid. It is useful in the detection of compounds of the heavy metals in solutions.

Sulphur chloride, S_2Cl_2 , is a yellow liquid with an offensive odor, the fumes of which are poisonous. It dissolves sulphur and is used in vulcanizing rubber.

EXERCISES

1. Prove that the formula of hydrogen sulphide is H_2S .
2. Why is the formula of sulphur chloride written S_2Cl_2 instead of SCl ?
3. How many liters of hydrogen sulphide can be obtained by

treating with hydrochloric acid 150 grams of a sample of impure iron sulphide containing 60 per cent by weight of FeS ?

4. How many liters of sulphur dioxide are produced when 12 grams of sulphur are burned with sufficient oxygen ($\text{S} + \text{O}_2 \rightarrow \text{SO}_2$)?

5. Prove that rhombic and prismatic sulphur are composed of the same substance.

6. Describe the different stages through which sulphur passes on being heated.

7. Why was it impossible to mine the Louisiana deposit of sulphur. How is the sulphur obtained from it?

8. What is the *lime-sulphur spray*? Why should it be made in the open air?

9. How could you find out whether a sample of water had dissolved lead from lead pipes through which it had been passed?

10. A solution is supplied to you that is known to contain either arsenic or antimony. How could you ascertain which was present?

11. Why do paintings blacken more quickly and silverware tarnish more rapidly in large cities than in the country?

12. Would you expect potted plants to thrive better in a house heated by a hot-air furnace or in one heated by hot water from a central source?

13. Compare the properties of water with those of hydrogen sulphide. What are some of the chief changes produced by the substitution of an atom of sulphur for one of hydrogen?

14. Write the formulas of 4 oxides and of the corresponding sulphides.

15. How many liters of air would be required (a) to burn 2 liters of hydrogen sulphide completely, (b) to burn only the hydrogen, liberating the sulphur? Assume that air contains one-fifth of its volume of oxygen.

16. How many grams would 10 liters of hydrogen sulphide weigh at standard conditions?

17. Enough carbon disulphide is burned to give 2 liters of carbon dioxide. How many liters of sulphur dioxide are produced at the same time? How many liters of oxygen are needed?

18. Why does a rubber band blacken a silver coin when the two are carried in the same pocket?

REVIEW QUESTIONS

1. Describe the manufacture of hydrochloric acid.
2. How is nitric acid made on a large scale?
3. What connection has the high boiling point of sulphuric acid with its use in the manufacture of nitric acid?

CHAPTER XXVIII

OXIDES AND ACIDS OF SULPHUR

SULPHUR DIOXIDE (SO_2)

309. Occurrence. Sulphur dioxide is a frequent by-product of volcanic eruptions, sometimes in enormous volumes causing great destruction. This was notably the case in the great eruption of 1783 in Iceland, when 9,000 human beings and 250,000 cattle were suffocated by sulphur-dioxide fumes.

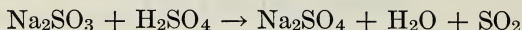
The sulphur that coal always contains is mostly liberated as sulphur dioxide when the coal is burned. Because of the great amounts of coal consumed in large cities, sulphur dioxide is always present in the air. Over 1,000 tons of sulphur dioxide is cast into the air of New York City daily by the burning of coal. The proportion of the gas varies from 1 part per million in the air of Central Park to 32 parts per million at times in the air of railroad tunnels.

We have seen that the sulphides of the heavy metals are important ores. In extracting a metal from a sulphide ore on a large scale the first step is to remove the sulphur by heating the ore in a current of air, when the sulphur combines with oxygen and escapes as sulphur dioxide. Enough sulphur dioxide is discharged into the air every year from the smelting plants of the United States to make 8,000,000 tons of sulphuric acid, which is more than our normal annual output.

310. Formation. Sulphuric acid, the most important of all chemical products, is made from sulphur dioxide. The enormous quantities of sulphur dioxide needed for this purpose are made by burning sulphur or by roasting the abundant brass-yellow mineral *pyrite*, which is *iron disulphide*, FeS_2 . When

pyrite is burned, the sulphur is oxidized to sulphur dioxide, which is led away and made into sulphuric acid, and the iron to *ferric oxide*, Fe_2O_3 , which remains behind as a red clinker. Thus ferric oxide becomes a by-product of the sulphuric-acid works.

Sulphites, like sodium sulphite, Na_2SO_3 (§ 162), liberate sulphur dioxide when treated with acids:



This behavior serves as a *test* to detect the sulphites and is sometimes used to prepare sulphur dioxide in the laboratory.

311. Preparation. Sulphur dioxide is prepared in the laboratory by heating concentrated sulphuric acid with copper in the form of turnings, tacks, or small nails:



The apparatus is similar to that used in the preparation of chlorine (Fig. 67). The sulphur dioxide is collected by downward displacement. Care is required, for the flask may break, and hot sulphuric acid makes a serious burn on the flesh.

312. Physical properties. Sulphur dioxide is a colorless, suffocating gas, with a characteristic sharp odor which is noticeable when sulphur is burned. Its specific gravity referred to air is 2.21. Water at 0° dissolves 80 times its volume of sulphur dioxide.

Sulphur dioxide is easily liquefied. At room temperature a pressure of $2\frac{1}{2}$ atmospheres is sufficient to convert it into a transparent liquid, and under the ordinary pressure of the air the gas is liquefied at -8° , a temperature which can be obtained by a mixture of ice and salt.

The liquefaction of sulphur dioxide in the laboratory is illustrated in Figure 172. The gas is generated by heating copper with sulphuric acid in *A*. It is cooled and dried by

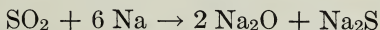
being bubbled through concentrated sulphuric acid in *B* and is then passed into the U-tube *C*, which is packed in a vessel containing ice and salt. The sulphur dioxide condenses in the U-tube to a colorless liquid.

Liquid sulphur dioxide comes into commerce in metal cylinders and in glass "siphon bottles." The liquid produces intense cold when it evaporates and is employed in some ice machines.

313. Chemical conduct.

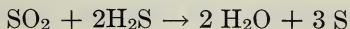
Sulphur dioxide resembles carbon dioxide in its behavior toward burning substances. All ordinary flames will be

quenched when lowered into a bottle of the gas. This is the explanation of the familiar method of extinguishing a fire in a chimney by burning sulphur at the bottom, so that the sulphur dioxide may ascend with the draft and come into contact with the burning soot. Sodium, however, burns brilliantly in sulphur dioxide to a mixture of sodium oxide and sodium sulphide:



and potassium acts in the same way.

When sulphur dioxide is mixed with hydrogen sulphide, both gases disappear, and water and sulphur are formed:



We have seen that both sulphur dioxide and hydrogen sulphide are discharged from volcanoes, and the reaction just mentioned is the cause of the tendency of sulphur deposits to occur in regions that are, or have been, the seats of volcanic activity.

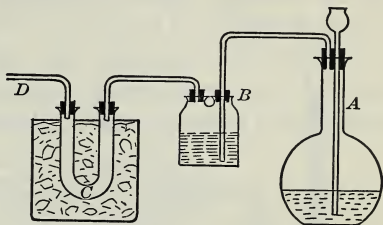


Fig. 172. Liquefaction of sulphur dioxide.

314. Formula of sulphur dioxide. Let us now examine the evidence on which the formula of sulphur dioxide is based. Figure 173 shows the method of determining the composition of sulphur dioxide *by weight*. A gentle stream of oxygen is passed through the apparatus in the direction indicated by the arrows. One gram of sulphur is burned in the little porcelain vessel *V*, and the sulphur dioxide produced is all absorbed by a concentrated solution of potassium hydroxide in the U-tube, which is weighed before and after the experiment. It will be found that the increase in weight of the U-tube is 2 grams. This means that 2 grams of sulphur dioxide have been formed.

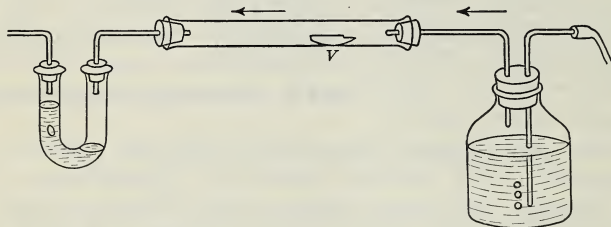


Fig. 173. Apparatus for determining the composition of sulphur dioxide by weight.

Thus, 1 part of sulphur by weight combines with 1 part of oxygen. As the atomic weight of sulphur is 32, 32 parts of sulphur would combine with 32 parts of oxygen. But the atomic weight of oxygen is 16, and 32 parts would make 2 *atoms*. Hence the *simplest formula* is SO_2 .

The specific gravity of sulphur dioxide referred to air is 2.21. Hence its molecular weight is 2.21×29 , or 64. The formula SO_2 , which corresponds to this molecular weight, is, therefore, correct.

Confirmation is obtained by the experiment of Figure 174. The retort is filled with oxygen and dips into mercury. The bit of sulphur at *A* is heated gently until it burns. At first the expansion due to heat drives the mercury down a little, but

when the retort cools, its level is the same as at first. *The oxygen has produced its own volume of sulphur dioxide.*

Since equal volumes of gases contain equal numbers of molecules, this means that *each molecule of oxygen has yielded a molecule of sulphur dioxide.* But each molecule of oxygen contains 2 atoms. Hence each molecule of sulphur dioxide must contain 2 atoms of oxygen.

We have just shown that the weight of the molecule of sulphur dioxide is 64. Subtracting 32 for the 2 oxygen atoms, we have left 32 for the sulphur. But since the atomic weight of sulphur is 32, this means 1 atom of sulphur. Hence, the formula of sulphur dioxide is SO_2 .

315. Effect on animals and plants. High percentages of sulphur dioxide in the air produce spasms of the respiratory apparatus which make breathing impossible, but the continual inhalation of air containing small quantities does not seem to produce bad results. The air of a copper smelting works is so highly charged with sulphur dioxide that the visitor finds it difficult to breathe, yet the furnacemen work in this atmosphere year after year without apparent damage.

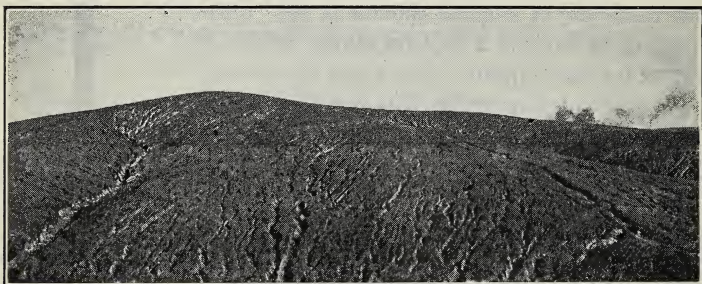
There is no question, however, that sulphur dioxide is a powerful poison to vegetation. Formerly, when it was the practice to remove a portion of the sulphur from copper ores by simply piling the ore, mixed with fuel, into a heap and setting fire to the mass, complete and widespread devastation to field and forest was wrought by the sulphur dioxide that escaped. At present the best practice is to roast the ores in a furnace, to dilute the gases from the furnace with air, and to discharge them from a number of stacks instead of from one. In California and Utah state laws provide that the gas that



Fig. 174. Apparatus for determining the formula of sulphur dioxide.

escapes from the stacks shall not contain more than 0.75 per cent by volume of sulphur dioxide. Serious damage to crops can hardly occur if this requirement is met.

316. Uses. The bleaching action of sulphur dioxide can be strikingly shown by dropping carnations or violets into a jar of the gas; the color will become much paler or will disappear entirely. The sulphur dioxide that is so largely employed for bleaching wool, silk, and straw is made by burning sulphur.



Courtesy of the Forest Service.

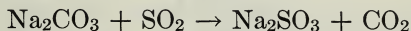
Fig. 175. A hillside once heavily wooded devastated by sulphur-dioxide fumes from heap roasting of copper ore.

In bleaching by chlorine or by hydrogen peroxide, the coloring matter is *oxidized* and destroyed. Sulphur dioxide, on the contrary, *reduces* the coloring matter, robs it of oxygen, and converts it into a colorless compound. Re-oxidation by the oxygen of the air may cause the color to return, so that bleaching by sulphur dioxide is not always permanent. This is the explanation of the gradual darkening of hat-straw under the influence of light and air.

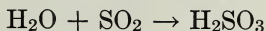
Sulphur dioxide is an excellent disinfectant, but because of its bleaching action on colored fabrics and its tendency to tarnish metal objects, it has been displaced by *formaldehyde* (§ 589), which disinfects even more thoroughly and does not bleach or affect the lustre of metals.

The fact that sulphur dioxide kills the bacteria that cause putrefaction has led to its employment for *preventing the decay or fermentation of food products*. It is used in increasing quantities in the preparation of such materials as table sirups, canned corn, canned cherries, and dried fruits, on which, in many cases, it acts both as a bleach and as a preservative. Whether this application of sulphur dioxide should be permitted is a debatable question.

The chief chemical use of sulphur dioxide is for the manufacture of sulphuric acid, for which purpose it is made in enormous quantities by burning sulphur itself or pyrite, FeS_2 . It is also used in the preparation of the sulphites, of which *sodium sulphite*, Na_2SO_3 , is the most important. Sodium sulphite is made by exposing moist sodium carbonate, Na_2CO_3 , to sulphur dioxide:



317. Sulphurous acid, H_2SO_3 . The behavior of sulphur dioxide toward water is similar to that of carbon dioxide. Chemical combination occurs when the sulphur dioxide dissolves, and the solution contains **sulphurous acid, H_2SO_3** :



Sulphurous acid is known only in solution. When the liquid is boiled, the sulphurous acid is decomposed again into sulphur dioxide and water, and the sulphur dioxide escapes.

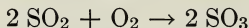
Sulphurous acid is the acid corresponding to sodium sulphite, Na_2SO_3 , and in general its salts are called the **sulphites**. Most of the sulphites of the metals are insoluble in water, potassium and sodium sulphite being the chief exceptions. The sulphites dissolve in hydrochloric acid with effervescence, giving off sulphur dioxide, which can be recognized by its odor.

Calcium hydrogen sulphite, $\text{Ca}(\text{HSO}_3)_2$, is of industrial importance. Its solution dissolves the cement that holds the

fibres of wood together and converts the wood into a pulp suitable for the *manufacture of paper*.

SULPHUR TRIOXIDE, SO_3

318. Preparation. *Sulphur trioxide* is produced by the union of each molecule of sulphur dioxide with an additional atom of oxygen:



This combination is slow, but at 400° , in presence of finely divided platinum, it becomes rapid enough to serve for the commercial production of sulphur trioxide.

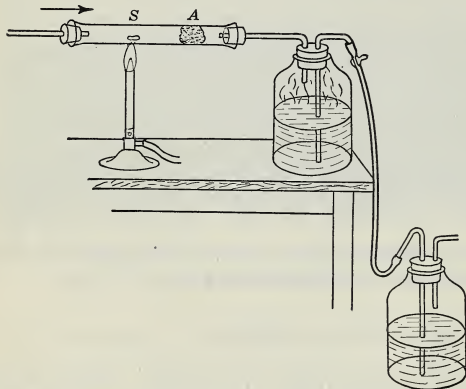
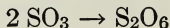


Fig. 176. Preparation of sulphur trioxide.

In Figure 176 is shown a laboratory illustration of the process. Sulphur burns to sulphur dioxide at *S*. By running water out of the bottle on the table enough air is drawn over the sulphur to provide an excess of oxy-

gen. At *A* is a wad of asbestos which has been coated with finely divided platinum. When this is gently heated, a dense, white cloud of sulphur trioxide appears in the upper bottle, where it is slowly absorbed by the water.

319. Properties. Freshly prepared sulphur trioxide is a colorless liquid. On preservation the SO_3 molecules unite in pairs to form double molecules S_2O_6 :



and the liquid is converted into a mass of silky needles resembling asbestos, which must be sealed up in glass bulbs to prevent air access.

When exposed to the air, sulphur trioxide gives off a dense, white, suffocating smoke and absorbs water from the air, passing into an oily liquid, which is **sulphuric acid**:



The same combination occurs with explosive violence when sulphur trioxide is dropped into water.

SULPHURIC ACID

320. Contact process. *Sulphuric acid*, the most important of all chemical products, is largely made from sulphur trioxide and water, the sulphur trioxide being obtained by the method just described. The procedure is called the “**contact**

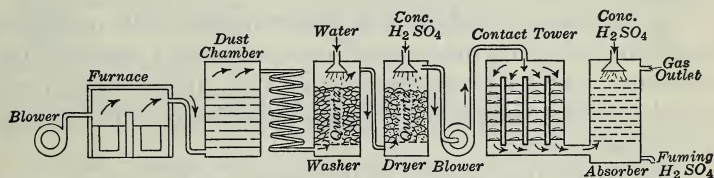


Fig. 177. Manufacture of sulphuric acid by the contact process.

process ” because the platinum acts simply by contact, without entering into the chemical process. In fact, if the platinum were consumed, the process could not be employed commercially, since platinum is far more expensive than gold.

A diagram of the contact process is given in Figure 177. A current of air is driven by the *blower* through the *burner* in which pyrite or sulphur is burned to sulphur dioxide. An excess of air is used, since additional oxygen will be needed later to convert the sulphur dioxide into sulphur trioxide.

The mixture of sulphur dioxide and air passes from the furnace through a *dust chamber*, in which the coarser dust is deposited, and is then cooled by traversing a long iron pipe. The gas is now passed in at the bottom of the *washer*, a tower packed with quartz, which is sprayed with water. As the gas passes upward through the quartz, in intimate contact with the water trickling downward, the remaining fine dust is removed. Since the gas is moist after this treatment, it must now be dried. The drying is effected in a similar tower packed with quartz over which trickles strong sulphuric acid.

The gas is now ready for the *contact tower*, in which asbestos coated with 10 per cent of its weight of finely divided platinum is spread out on perforated shelves, through which the gas slowly passes in a downward direction. Here the combination of the sulphur dioxide and oxygen is brought about. The gas that leaves the contact apparatus is a suffocating mist, consisting of air in which are suspended countless little drops of sulphur trioxide.

In the *absorber*, which is a tower packed with quartz or acid-proof tile, this mist passes upward against concentrated sulphuric acid trickling downward. The sulphuric acid completely absorbs the sulphur trioxide from the air, which is now permitted to escape.

The liquid that collects in the bottom of the absorber is a fuming solution of sulphur trioxide in sulphuric acid. By cautiously adding to this the proper quantity of water, 100 per cent sulphuric acid can at once be prepared.

321. The lead-chamber process. When sulphur dioxide, oxygen, and water are left in contact, sulphuric acid is slowly formed:



In the presence of *nitrogen peroxide*, which acts as a catalyst, the formation of sulphuric acid is greatly accelerated and becomes rapid enough to serve as the basis of a process by which

millions of tons of sulphuric acid are made annually. This is the **lead-chamber process**, so-called because the gases are confined in great rectangular chambers constructed of thin plates of lead, the cheapest material available that will withstand the corrosive action of sulphuric acid.

A diagram of the lead-chamber process is given in Figure 178. The sulphur dioxide is made as in the contact process, by burning sulphur or pyrite in a current of air. The hot gases from the furnace pass upward through the *Glover tower*,

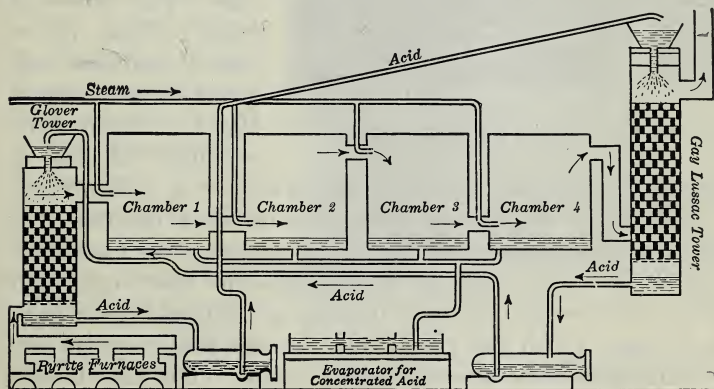


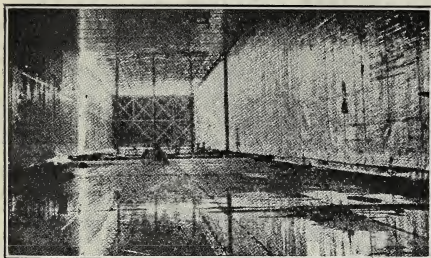
Fig. 178. Manufacture of sulphuric acid by the lead-chamber process.

which is a tower 30 ft. or more in height, made of lead lined with fire brick and packed full of rings of acid-proof tile. The main object of the Glover tower is to add nitrogen peroxide to the gases. This is done by spraying in at the top of the tower a solution of nitrogen peroxide in concentrated sulphuric acid, obtained from the *Gay-Lussac tower*.

As this solution trickles down over the acid-proof rings, which are kept hot by the gases from the furnace, the nitrogen peroxide bubbles out of its solution in the sulphuric acid, mixes with the gases ascending in the tower, and is swept with them into the first lead chamber, where the deposition of the sul-

phuric acid begins. The other chambers continue the process and push it to completion. Short, wide lead tubes carry the gases from one chamber to the next. The necessary water is

introduced into the chambers in a fine spray or as steam.



Courtesy of the Bureau of Mines.

Fig. 179. Interior of a lead chamber.

The sulphuric acid falls like rain to the bottom of the chambers. The excess of water dilutes it, so that it contains only about 60 per cent of H_2SO_4 . From time to time the acid is

run off through tubes into a lead reservoir or a concentrator.

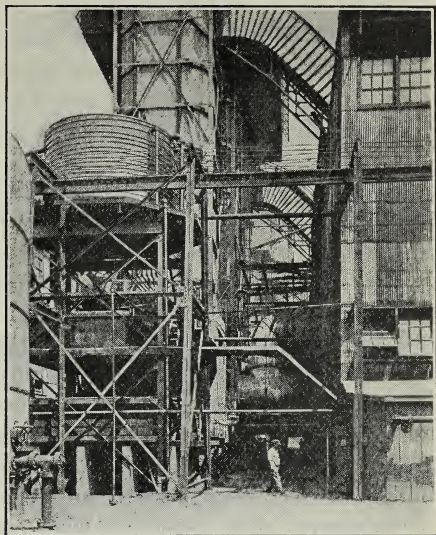
322. Since the nitrogen peroxide is merely a catalyst, it is not consumed in the lead chambers, and since it is expensive, it must be saved from the waste gases and used again and again. This is the important function of the *Gay-Lussac tower*, up through which the gases from the last lead chamber are passed before they are allowed to escape. The Gay-Lussac tower is 30 to 60 ft. high and is constructed of lead plates. It is packed with acid-proof tile over which is sprayed concentrated sulphuric acid. This absorbs the nitrogen peroxide, so that the gases that pass from the top of the Gay-Lussac tower to the chimney are almost free from it.

The solution of nitrogen peroxide in concentrated sulphuric acid that collects at the bottom of the Gay-Lussac tower is pumped to the top of the Glover tower and sprayed over the rings of acid-proof tile as already described. Small quantities of nitric acid are added at the top of the Glover tower from time to time to make up for the unavoidable losses of nitrogen peroxide.

Sulphuric acid from the lead chambers, containing 60 per

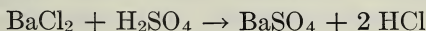
cent of water, is also sprayed in at the top of the Glover tower. In spite of this the acid that collects at the bottom of the tower is quite concentrated (80 per cent), for much water is boiled out of it in trickling over the hot acid-proof tile rings. It is ready to be pumped to the top of the Gay-Lussac tower for use in absorbing the nitrogen peroxide out of the waste gases.

323. Test for sulphuric acid. A solution of *barium chloride*, BaCl_2 , produces in a solution containing sulphuric acid a white precipitate of *barium sulphate*, BaSO_4 :

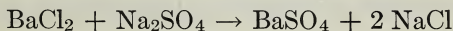


Courtesy of the Davison Chemical Co.

Fig. 180. Towers and pipe connections to chambers in a modern lead-chamber plant.

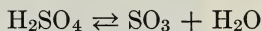


A solution containing a *sulphate*, like *sodium sulphate*, Na_2SO_4 , also responds to the test:



The barium-chloride test, therefore, does not distinguish between *free sulphuric acid* and a *sulphate*. This distinction can be made by adding a little *sugar* to the original liquid and evaporating to dryness at a gentle heat. *Free* sulphuric acid blackens the sugar, leaving a mass of charcoal. A solution containing a sulphate does not show this effect.

324. Physical properties. Pure sulphuric acid, often called oil of vitriol, is a colorless oily liquid. It is nearly twice as dense as water, its specific gravity being 1.84. It boils at 338°, and the boiling is accompanied by a slight decomposition into sulphur trioxide and water:

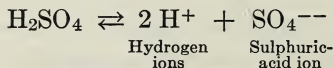


The vapor emitted by heated sulphuric acid is suffocating and should not be allowed to escape into the air of the laboratory.

Sulphuric acid can be mixed with water in any proportion without the formation of two layers. Much heat is liberated when the two liquids come together, and *in diluting sulphuric acid the acid must be poured in a thin stream into the water, never the water into the acid.* The attraction of sulphuric acid for water is so great that when exposed in a beaker the acid will double its volume in a few days by absorbing water from the air. Gases are often dried in the laboratory by allowing them to bubble through concentrated sulphuric acid.

Sulphuric acid explodes when mixed with concentrated ammonia. When concentrated sulphuric and hydrochloric acids are mixed, both liquids are thrown violently out of the vessel. Energetic explosions result when sulphuric acid is poured over potassium chlorate. It is quite dangerous, therefore, to mix concentrated sulphuric acid thoughtlessly with other chemicals in the laboratory.

325. Behavior with water. The heat produced when sulphuric acid is mixed with water is partly due to the ionization of the acid:

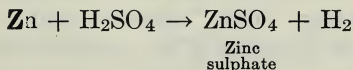


We have seen that *sugar* is charred by sulphuric acid. The formula of sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, shows that it contains hydrogen and oxygen in the proportions in which these two elements

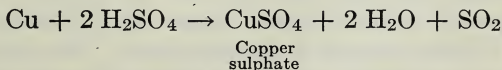
exist in water. Under the influence of sulphuric acid the hydrogen and oxygen are removed as water, while carbon in the form of charcoal remains.

Wood behaves in a similar way with sulphuric acid, as can be shown by stirring a little sulphuric acid in a test-tube with a splint. Its action on paper can be illustrated by writing a word with a glass rod dipped in dilute sulphuric acid and then warming the paper gently. As the water evaporates, the sulphuric acid becomes concentrated, and the word is charred upon the paper. The brown color which commercial sulphuric acid often possesses is due to this charring action upon dust containing particles of wood, paper, etc., which falls into the acid.

326. Action upon metals. Dilute sulphuric acid rapidly dissolves active metals, like iron, zinc, and magnesium:



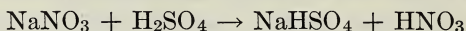
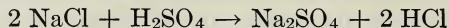
Upon the less active metals, like copper, mercury, and silver, dilute sulphuric acid has little action, but hot concentrated sulphuric acid rapidly produces the sulphate, with escape of sulphur dioxide:



The noble metals, platinum and gold, are unaffected by sulphuric acid, even when hot and concentrated. Iron, which is quickly dissolved by dilute sulphuric acid, is not attacked by concentrated sulphuric acid, which is therefore usually shipped in iron tank cars. This is far cheaper, safer, and more convenient than shipment in glass containers. The widespread use of concentrated sulphuric acid in chemical industry is partly due to the accident that it has no action upon iron and

can therefore be transported more cheaply than can acids that must be shipped in glass bottles or carboys.

327. Action upon salts. The action of sulphuric acid upon sodium chloride and upon sodium nitrate has been studied in detail:



These are typical cases. The usual action of sulphuric acid upon a salt is to *liberate the other acid*, at the same time forming a sulphate. The connection of the high boiling point (338°) of sulphuric acid with this behavior is explained in our discussion of nitric acid (§ 247).

328. Sulphuric acid in industry. We have seen that the sulphuric acid obtained from the lead chambers contains about 40 per cent of water. This "chamber acid" is cheap and is used whenever the presence of the water is not objectionable. The largest single use of the chamber acid is in treating *phosphate rock* to convert it into *superphosphate fertilizer*, but considerable quantities are also consumed in the manufacture of the three great industrial sulphates, *ammonium sulphate*, *aluminum sulphate*, and *sodium sulphate*. Rust and scale are removed from iron and steel castings by dipping them into dilute sulphuric acid, a process known as "pickling," which consumes a large tonnage of chamber acid. The liquid in the ordinary storage battery consists of dilute sulphuric acid.

Another set of industries demand sulphuric acid *free from water*, practically 100 per cent pure. Such an acid is supplied directly by the contact process, or it can be made by heating the chamber acid in pans of acid-proof iron; the water evaporates, and the sulphuric acid, owing to its high boiling point, remains. The largest use of concentrated sulphuric acid is in the refining of petroleum, from which it removes substances which would produce an unpleasant odor in burning. Other

important applications are in the manufacture of explosives, like nitroglycerine and guncotton, and in the preparation of dyestuffs. The normal annual production of sulphuric acid in the United States is 4,000,000 tons, but during the World War this output was doubled.

329. The sulphates. The salts in which the hydrogen of sulphuric acid is replaced by metals are called the **sulphates**. They are described in the chapters devoted to the corresponding metals. A brief tabular summary of some important sulphates is given here for reference:

IMPORTANT SULPHATES

Name	Formula	Common Name	Color	Uses
ALUMINUM SULPHATE.	$\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$	Sulphate of alumina	White	Purification of water, dyeing, sizing paper, etc.
AMMONIUM SULPHATE.	$(\text{NH}_4)_2\text{SO}_4$	Sulphate of ammonia	White	Fertilizer, manufacture of ammonium chloride
BARIUM SULPHATE. . . .	BaSO_4	Barytes	White	Paint, filler for paper and for rubber tires
CALCIUM SULPHATE. . .	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	Gypsum	White	Paint, fertilizer, making plaster of Paris
COPPER SULPHATE. . . .	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	Bluestone or Blue vitriol	Blue	Fungicide, electric batteries, electrotyping copper refining
FERROUS SULPHATE. . .	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	Green vitriol	Green	Disinfectant, making ink, calico printing

SUMMARY

Sulphur dioxide, SO_2 , is obtained in the laboratory by heating copper with concentrated sulphuric acid. On a large scale it is made by burning, in a current of air, sulphur or pyrite, FeS_2 .

Sulphur dioxide is used in bleaching wool, straw, and silk, as a food preservative, and in the manufacture of sulphuric acid.

Sulphur trioxide, SO_3 , is formed by the union of sulphur dioxide with oxygen. It combines with water, forming sulphuric acid.

Two methods of manufacturing sulphuric acid are in use. In both the first step is the production of a mixture containing sulphur dioxide and oxygen, by burning sulphur or pyrite in an air current that supplies about twice as much air as is necessary for the combustion.

In the **contact process** the mixture of sulphur dioxide and oxygen is passed over finely divided platinum, whereupon sulphur trioxide is formed. This is absorbed in concentrated sulphuric acid, and by adding the calculated quantity of water the liquid is converted into 100 per cent sulphuric acid.

In the **lead-chamber process** the mixture of sulphur dioxide and oxygen is passed into large chambers of sheet lead, where it comes into contact with *steam* and *nitrogen peroxide*, NO_2 . The latter acts as a catalyst in bringing about the union of the sulphur dioxide, oxygen, and water to sulphuric acid.

EXERCISES

1. Each year over 5,000,000 tons of sulphur dioxide are thrown into the air from the stacks of smelting plants in the United States, while at the same time pyrite is imported and burned to make sulphuric acid. From the standpoint of the conservation of our national resources what is the remedy for this situation?

2. Sketch briefly (a) the contact process, (b) the lead-chamber process. Which process of making sulphuric acid would be suitable for a corporation engaged in making dyestuffs? For a concern operating coke ovens that makes ammonium sulphate as a by-product? For a large glass works needing sodium sulphate? For a manufacturer of superphosphate? For an oil refinery? For a maker of high explosives? Why?

3. Compare chlorine and sulphur dioxide as bleaching agents.

4. Why has formaldehyde displaced sulphur dioxide as a disinfectant?

5. A beaker containing concentrated sulphuric acid is sometimes

placed inside the case of a balance. Why? Why is the beaker never more than one-fourth filled?

6. Either sulphuric or hydrochloric acid can be used in the preparation of hydrogen sulphide, but only sulphuric acid can be employed in making nitric acid. Why?

7. How can a farmer ascertain whether a material supplied to him is ammonium sulphate or not?

8. Exactly what would happen if a solution of *barium chloride* were added to one of *silver sulphate*? Would anything remain in solution if the quantities of the two salts were properly adjusted?

9. Sulphuric acid has been called "the foundation of chemical industry." Why?

10. An automobile mechanic needs a supply of a mixture of 1 gallon of concentrated sulphuric acid and 3 gallons of distilled water for filling storage batteries. Explain exactly how the sulphuric acid should be diluted.

11. Why is a glass vessel liable to become overheated and crack when sulphuric acid is heated in it? Remembering that all parts of the body contain abundant water, explain the serious effect of hot, concentrated sulphuric acid upon the skin.

12. A student has two bottles both labelled "sulphuric acid," but in one the acid is concentrated and in the other dilute. How can he distinguish them?

13. How are the formulas of the *sulphides*, *sulphites*, and *sulphates* related? How could you test a substance to ascertain whether it was a sulphide, a sulphite, or a sulphate?

14. Why does a straw hat slowly darken again after it has been bleached?

15. Explain the precise difference in meaning between the formulas SO_3 and S_2O_6 .

16. How many grams of sulphur trioxide are formed when 5 grams of sulphur are burned with an excess of air and the combustion products passed over finely divided platinum?

17. How many liters of air are needed to burn 500 grams of sulphur to sulphur dioxide? Assume that air contains 21 per cent by volume of oxygen.

18. How many tons of sulphuric acid can be made from 40 tons of pure pyrite, FeS_2 ?
19. How many tons of sulphuric acid can be made from 40 tons of pure sulphur?
20. How many tons of sulphuric acid can be made from 100 tons of impure pyrite containing 48 per cent of sulphur?
21. If the specific gravity of sulphuric acid is 1.84, how many grams of sulphur are there in 100 c.c. of it?

REVIEW QUESTIONS

1. What is meant by *atomic weight*? Is it a chemical constant or a physical constant? How would you determine the atomic weight of copper?
2. Suppose you had a cube of pure copper the edge of which measured 2 cm. and found it to weigh 71.2 grams, could you calculate the *specific gravity* of copper from your results? Could you draw any conclusion about the *atomic weight* of copper?
3. What is molecular weight, and how is it determined? Explain what is meant by the statement that the atomic weight of sulphur is 32, and its molecular weight 256.

Helium is one of the chemically inactive gases of the argon group; lithium is a metal very similar to sodium; fluorine is a gas which resembles chlorine very closely and is the most active of all the non-metals. The elements between lithium and fluorine are intermediate in character: any element is less metallic than the element to the left of it. Thus, in passing from lithium to the right there is a gradual loss of metallic properties, which finally, when we arrive at fluorine, is complete.

Now the next element in order is neon ($\text{Ne}=20$), another of the inert gases of the argon group. There is no gradual transition from fluorine to neon. We pass at once from the most active non-metal to a completely inactive element. After neon comes sodium ($\text{Na}=23$), one of the most positive of the metals. There can be no doubt that sodium belongs in the same group as lithium, for the two resemble each other in a remarkable way. This is true also of the elements that follow sodium in the second line. Each is like the one above it in the first line: magnesium is similar to glucinum, aluminum to boron, and so on. This similarity is greater at the ends than in the middle of the table. Sodium is more similar to lithium, and chlorine to fluorine, than aluminum is to boron, or silicon to carbon. Yet the similarity between these middle pairs of elements is great enough to show that they belong together.

333. The Periodic Law. Thus these two sets of 8 elements each exhibit a relationship like that of two octaves of notes in music:

Octave 1: **C D E F G A B C**

Octave 2: **c d e f g a b c**

In fact, when this remarkable arrangement of the elements was first brought forward, it was called the "**law of octaves**" for that reason. *The properties of the elements change with increasing atomic weight, and the change is a periodic one*—that is, similar elements occur again and again as the atomic weight

us in classing chromium with oxygen and sulphur, and manganese with fluorine and chlorine. One important difference between this arrangement and that of the short periods is, then, that at the element numbered VII—manganese in this case—the metallic properties have partially, but by no means completely, disappeared. Further, the next metal, iron, is by no means an inert gas like argon, as it should be if it stood at the beginning of a new short period. The 3 elements of the column numbered VIII—iron, nickel, and cobalt—resemble each other strongly. Copper is not nearly as positive a metal as potassium. In the last 7 elements, from copper to bromine ($\text{Br}=80$), there is a gradual and complete disappearance of the metallic characteristics. Bromine is an unmistakable non-metal and belongs in the same group as fluorine and chlorine.

This set of 18 elements is called the *first long period*. The general plan on which a long period is built is this. First stands one of the inert gases of the argon group, and second one of the active metals of the sodium group. In the following 6 elements the metallic qualities diminish, but do not completely disappear, so that the element numbered VII, manganese, for instance, shows mixed metallic and non-metallic characters. The position of the 3 following elements is peculiar. Their atomic weights lie near together (compare the atomic weights of iron, nickel, and cobalt), and they resemble each other strongly. Finally, through the remaining 7 elements the metallic properties gradually and completely vanish, so that the last member of the long period is, in all respects, a non-metal.

335. Grouping of the elements according to the Periodic Law. The complete arrangement of the elements according to the Periodic Law is given in the table on pages 392 and 393. The vertical columns are called **groups**, and the student will be prepared to find that elements in the same group resemble each other. It is convenient to divide most of the groups into two

PERIODIC ARRANGEMENT

PERIODS	GROUP 0	GROUP I		GROUP II		GROUP III	GROUP IV	
	THE INERT GASES	SODIUM FAMILY	COPPER FAMILY	CALCIUM FAMILY	ZINC FAMILY	BORON, ALUMINUM, AND RARE ELEMENTS	CARBON FAMILY	TIN FAMILY
1	Helium He = 4	Lithium Li = 7		Glucinum Gl = 9		Boron B = 11	Carbon C = 12	
2	Neon Ne = 20	Sodium Na = 23		Magnesium Mg = 24		Aluminum Al = 27	Silicon Si = 28	
3	Argon A = 40	Potassium K = 39		Calcium Ca = 40		Scandium Sc = 45	Titanium Ti = 48	
		Copper Cu = 63.5		Zinc Zn = 65.5		Gallium Ga = 70	Germanium Ge = 72.5	
4	Krypton Kr = 83	Rubidium Rb = 85.5		Strontium Sr = 87.5		Yttrium Yt = 89	Zirconium Zr = 90.5	
		Silver Ag = 108		Cadmium Cd = 112		Indium In = 115	Tin Sn = 119	
5	Xenon X = 130	Caesium Ca = 133		Barium Ba = 137		Lanthanum La = 139	Cerium Ce = 140	*
		Gold Au = 197		Mercury Hg = 200		Thallium Tl = 204	Lead Pb = 207	
6	Niton Nt = 222			Radium Ra = 226			Thorium Th = 232	

* Between cerium and tantalum in the third long period lie 12 elements classified as *rare earth metals* with atomic weights ranging from 141 (praseodymium) to 175

OF THE ELEMENTS

PERIODS	GROUP V		GROUP VI		GROUP VII		GROUP VIII
	RARE ELE- MENTS	NITROGEN FAMILY	CHRO- MIUM FAMILY	OXYGEN FAMILY	MAN- GANESE	CHLORINE FAMILY	IRON FAMILY PLATINUM FAMILY
1		Nitrogen N = 14		Oxygen O = 16		Fluorine F = 19	
2		Phosphorus P = 31		Sulphur S = 32		Chlorine Cl = 35.5	
3		Vanadium V = 51	Chromium Cr = 52		Manganese Mn = 55		Iron Fe = 56 Nickel Ni = 58.7 Cobalt Co = 59
		Arsenic As = 75		Selenium Se = 79		Bromine Br = 80	
4		Columbium Cb = 93	Molybdenum Mo = 96				Ruthenium Ru = 102 Rhodium Rh = 103 Palladium Pd = 107
		Antimony Sb = 120		Tellurium Te = 127.5		Iodine I = 127	
5		Tantalum Ta = 181.5	Tungsten W = 184				Osmium Os = 191 Iridium Ir = 193 Platinum Pt = 195
		Bismuth Bi = 209					
6		Uranium U = 238					

(lutecium). They have not yet been accurately studied and their position in the table is somewhat uncertain.

sub-groups known as **families**, and the resemblance between members of the same family is especially close. Thus, in Group I, the members of the *sodium family*—lithium, sodium, potassium, rubidium, and caesium—resemble each other far more than they resemble the elements of the *copper family*—copper, silver, and gold. The elements of Group O are all inert gases; those of Groups I and II are all metals, and so are all those of Group III except boron. With this exception, the non-metals are all contained in Groups IV, V, VI, and VII; the most active non-metals stand at the top, for, in a family composed of non-metals, the non-metallic properties decrease with increase of atomic weight. This is well shown by the fact that no non-metal is known having a higher atomic weight than that of tellurium ($\text{Te}=127.5$). In a family of metals, the reverse is usually true—the higher the atomic weight, the more marked the metallic properties.

The sodium group contains those elements which, from the chemical point of view, manifest metallic properties in the greatest perfection. The most positive metal of these, and, in fact, the most active metal known, is caesium ($\text{Cs}=133$), which has the highest atomic weight in the group.

336. Prediction of elements. The student will notice at once that there are many gaps in the table. A gap arises when we are forced to leave a vacant space for the sake of preserving the arrangement. Thus, in the second long period, after molybdenum ($\text{Mo}=96$) in the sixth group, the next known element in order of increasing atomic weight is ruthenium ($\text{Ru}=102$). Now the whole chemical character of this element shows that it belongs in the eighth group and not under manganese. Further, if we simply proceed in order, placing ruthenium under manganese, not only ruthenium itself, but every following element would be thrown out of place, and the whole latter portion of the table would be disarranged. Hence we leave a vacant space and preserve the arrangement, believing

that the place under manganese belongs to some unknown element which has an atomic weight of about 100. Thirty years ago, when the table was first published, gaps were more numerous. The Russian chemist *Mendelejeff*, the originator of the Periodic Law, gave it as his opinion that the vacant spaces would be filled by the discovery of new elements. In several cases he predicted in detail the properties of these elements and their principal compounds, from the place that they ought to occupy in the table. These predictions were verified many years later, the properties of the newly discovered elements agreeing with Mendelejeff's original statements with wonderful closeness—a striking proof that the periodic classification is a real law of nature and not a mere artificial arrangement.

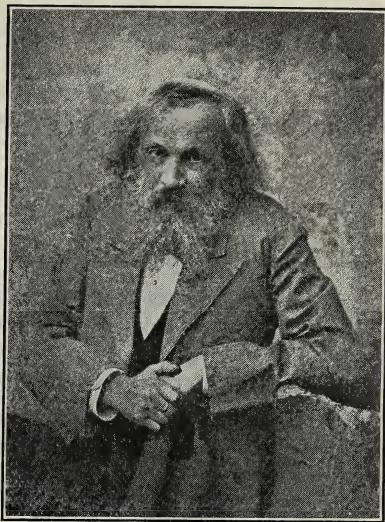


FIG. 181. DIMITRI IVANOVITCH
MENDELEJEFF (1834–1907).

Russian chemist, professor of chemistry in the University of St. Petersburg; advanced and established the Periodic Law and predicted from the periodic table the existence of several elements since discovered.

The method employed by Mendelejeff in predicting the properties of undiscovered elements may be made clear by an imaginary example.

Suppose that *sodium* were unknown. There would then be a vacant space in the periodic table in Group I, between lithium and potassium. In the horizontal series the gap would occur in the second short period, between neon and magnesium.

The atomic weight of the unknown element should be approximately the mean of its two vertical neighbors:

$$\begin{array}{ccc} \text{Li} & & \text{K} \\ 7 & + & 39 = 46 \\ & & 46 \div 2 = 23 \end{array}$$

or, the mean of its two horizontal neighbors:

$$\begin{array}{ccc} \text{Ne} & & \text{Mg} \\ 20 & + & 24 = 44 \\ & & 44 \div 2 = 22 \end{array}$$

Since in this family the melting point falls with increasing atomic weight, the melting point of the unknown element will be somewhere between that of lithium (186°) and that of potassium (63°). We predict roughly that the unknown element would melt at a temperature not far from 100° .

Its physical and chemical properties would resemble those of lithium and potassium. It would be soft enough to be cut with a knife, would burn readily when heated, and would communicate a marked color to the flame of the Bunsen burner. It would lose its lustre instantly in moist air and interact rapidly with water, liberating hydrogen and forming a hydroxide, which would be an active base.

The working out of the further details of the prediction may be left as an exercise to the student. It can be extended to the prediction of the properties, not only of the unknown element, but also of its compounds.

The Periodic Law is not yet an altogether complete and perfected classification of the elements. It is still in its formative stage. In pointing out profitable subjects for research and in fixing the true values of the atomic weights, it has been of great value to our science. The future may modify it in important details, but the fundamental fact that *the properties of the elements are periodic functions of their atomic weights* will remain.

SUMMARY

When the elements are arranged in the order of increasing atomic weights, elements of similar properties appear at definite intervals. In this way is obtained the **periodic table**, in the horizontal series of which the properties change gradually. The vertical groups contain elements that resemble each other. Most of the groups contain two families, and elements belonging to the same family resemble each other quite closely.

EXERCISES

1. What is *classification* of the elements? What are its advantages?

2. Look up the meaning of the word *periodic*. Why is this word applied to the classification of the elements?

3. Predict the physical properties of *lithium* from its place in Group I of the table. How would it behave with water? What is its valence? Write the formulas of its chloride, nitrate, and sulphate.

4. With what kind of element does each series begin? What kind of element forms the *second* member of each series (Group I)? With what kind of element does each series end?

5. Trace in detail the gradual disappearance of the metallic properties in the second period.

6. Is caesium a metal or a non-metal? It explodes when dropped into water. Is this fact surprising or to be expected? Write the formula of *caesium hydroxide*. Is it an acid, a base, or a salt? Would you handle it with the fingers? Why? Write the formulas of caesium chloride, nitrate, and sulphate.

7. Write the formulas of the oxide, chloride, nitrate, and sulphate of glucinum and of strontium.

8. Why would you expect gallium and indium to be *metals*? What familiar metal would they most resemble? Write the formulas of four compounds of gallium and of four compounds of indium.

9. How would platinum differ in behavior from rubidium (a) when exposed to the atmosphere; (b) when heated in air; (c) when placed in water?

10. What is meant by the statement that the inert gases have a valence of *zero*? How has this been proved?

11. What is a *period*? A *group*? A *family*?

12. What metals are most closely related to sodium? To copper? To tin? To zinc?

13. What elements are classed in the table with chlorine? With oxygen? With nitrogen?

CHAPTER XXX

GROUP I B. THE COPPER FAMILY

COPPER, SILVER, GOLD

337. General. Although the metals copper, silver, and gold occur in Group I of the periodic system along with the Sodium Family, they are quite different from the latter, being typical *heavy metals*, ductile, malleable, and tenacious, and slightly, or not at all, affected by air and water. They are much denser than the metals of the Sodium Family, copper, the lightest, being nearly 9 times as dense as water. Unlike the metals of the Sodium Family, the metals of the Copper Family were known to the ancients; they have been used from the earliest times for coinage and for jewelry. Copper was employed long before iron for weapons and other cutting implements.

COPPER ($\text{Cu} = 63.5$)

338. Occurrence. Copper occurs *native* in immense quartz deposits in northern Michigan, on the shore of Lake Superior. A single mass of copper found in one of the mines of this locality weighed 500 tons.

The most important ores of the metal are listed in the table on the next page.

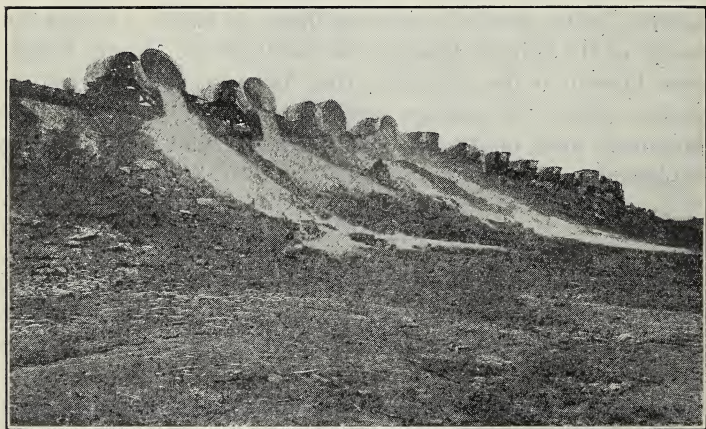
More than half the copper output of the world is obtained in the United States. The copper is mined chiefly in Arizona, Montana, Michigan, and Utah.

Small quantities of copper occur in animal and plant substance. Chocolate and cocoa contain 1 part of copper in 100,000 parts by weight, and it is found in the colored feathers

ORES OF COPPER

Scientific Name	Miners' Name	Formula	Color
CHALCOPYRITE	Copper pyrites	CuFeS_2	Golden yellow
CHALCOSITE ..	Copper glance	Cu_2S	Blackish gray
BORNITE	Purple copper ore, peacock ore	Cu_5FeS_4	Purplish black, iridescent when tarnished
CUPRITE	Red copper ore	Cu_2O	Red
MALACHITE.....		$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	Bright green

of some birds and in the blood of oysters, lobsters, scorpions, and cuttle-fish.



Courtesy of the "Scientific American."

Fig. 182. Slag is the waste product of all smelting operations; this is the slag dump of a copper smelter.

339. Extraction. The copper ores containing sulphur—*chalcopyrite*, *chalcosite*, and *bornite*—are by far the most important. Mixed with fuel (coke) and with a flux rich in silica, SiO_2 , they are charged into a vertical shaft furnace, similar in

principle to the iron blast furnace (§ 534), near the bottom of which a blast of air enters. Here some of the sulphur is oxidized and escapes as sulphur dioxide; some of the iron also is oxidized, and the iron oxide combines with silica to form iron silicate, which passes into the slag.

At the bottom of the blast furnace a dense metallic mass called "**matte**" collects, which contains about half its weight of copper, the balance being mainly sulphur and iron. The matte is run, still liquid, into the *converter* (Fig. 183), an egg-shaped vessel lined with brick made of pure sand which has a perforated false bottom. Here a blast of air is blown through the hot, liquid matte.

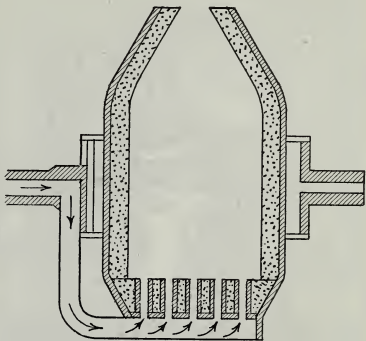
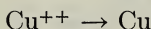


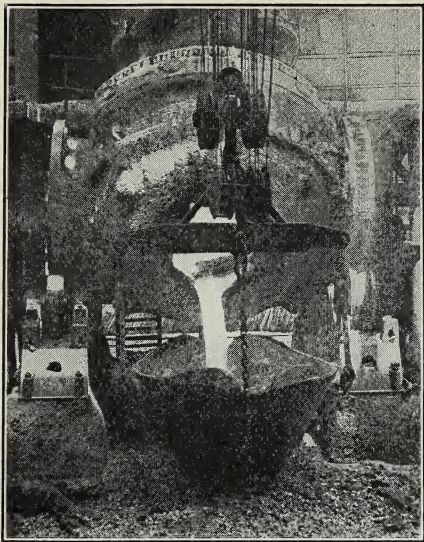
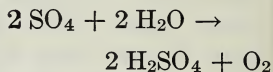
Fig. 183. Bessemer converter.

In the converter the process begun in the blast furnace is finished. The remaining sulphur is eliminated as sulphur dioxide, and the balance of the iron oxidizes, combines with the sand of the converter lining, and goes into the slag which covers the melted copper. When the operation is finished and the slag poured off, the metal, which is now called "**blister copper**" and is about 98 per cent pure, is cast into blocks about a yard square and 3 in. thick, which are sent to the refinery for further purification.

340. Electrolytic refining. When two electric-light carbons connected with the opposite poles of a battery (Fig. 185) are placed in a solution of copper sulphate, CuSO_4 , the negative carbon becomes coated with copper:



At the positive pole *oxygen* escapes. The blue color of the solution is due to the copper ions and it disappears when they are all removed. The liquid that remains after the experiment is simply dilute sulphuric acid. We may consider that the SO_4^{--} ion has given up its negative charge to the positive carbon and has at once attacked a molecule of water, forming sulphuric acid and oxygen:



Courtesy of the "Scientific American."

Fig. 184. Pouring blister copper from the converter.

as before, but no gas bubbles form at the anode, and the liquid shows no loss of color.

Upon reweighing the electrodes after the electrolysis, the cause of the different behavior of carbon and copper as anodes becomes clear. The copper anode has lost just as much as the cathode has gained. For every ion Cu^{++} that gave up its double charge at the cathode and became

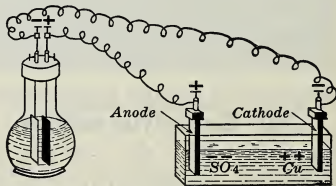


Fig. 185. Electrolysis of copper-sulphate solution.

ordinary copper, a copper atom from the anode took up a double charge and went into the liquid as an ion Cu^{++} . The net result is that copper is simply transferred through the solution from the positive to the negative plate. This behavior is the basis of the **electrolytic refining** of copper.

Because of the large demand for pure copper for electrical purposes, the refining of the metal is a great industry. The blocks of blister copper about 3 ft. square by 3 in. thick from the smelting works are suspended in a lead-lined wooden vat and made the anodes (A, A, A) in a solution of copper sulphate (Fig. 186). The liquid is kept in circulation

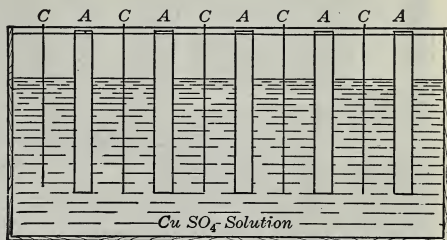


Fig. 186. Diagram of electrolytic copper refining.

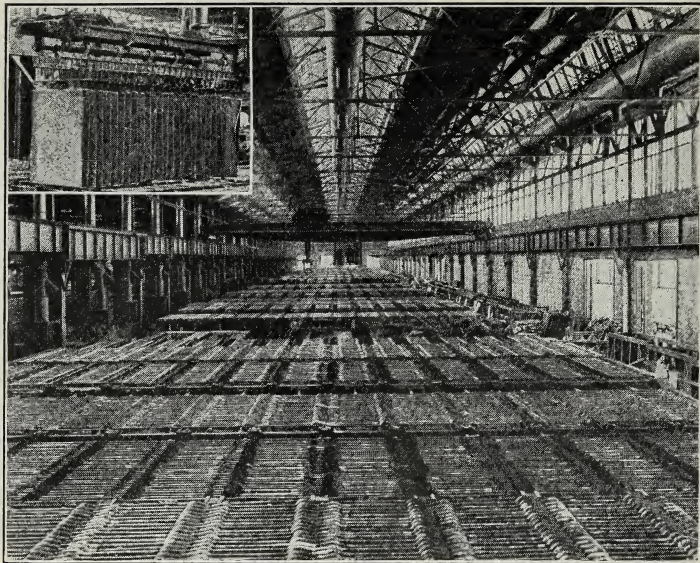
during the process. The cathodes (C, C, C) are thin plates of refined copper. The current comes from a dynamo and has a pressure of 0.2 volt. The copper dissolves at the anode and deposits at the cathode so thoroughly purified that it contains less than 0.1 per cent of foreign substances.

There are two classes of impurities in the blister copper:

1. Metals *more* active than copper, like iron and zinc. These dissolve at the anode but do not deposit at the cathode. They accumulate in the liquid, which is finally discarded to get rid of them.

2. Metals *less* active than copper, that is, noble metals, especially gold and silver, which are associated with the copper in small quantities in nearly all sulphide ores. Because of their inactivity these do not dissolve. They remain clinging to the anode, and as the latter disintegrates, they fall to the bottom of the tank, forming the so-called "mud." This is from time to time removed and worked up into **bullion**, which

goes to the Mint or to the manufacturing jeweler. The value of the gold and silver obtained is great enough to pay the whole expense of the refining process. Over \$100,000,000 worth of copper is now refined annually in the United States.



Courtesy of the Raritan Copper Works.

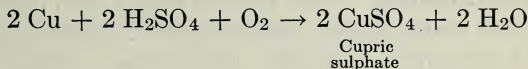
Fig. 187. Electrolytic tank room of a copper refinery. Inset: cathodes drawn from tank.

341. Physical properties. Copper is a red metal with a specific gravity of 8.9, which, although it has only half the toughness of iron, is still sufficiently strong for many structural purposes. It is quite malleable and ductile. Pure copper is an excellent conductor of heat, and it is excelled only by silver in conductivity for the electric current. Copper melts at $1,083^{\circ}$ and the liquid boils at $2,100^{\circ}$.

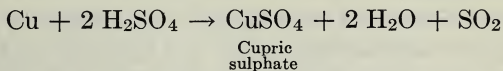
342. Chemical conduct. Copper when heated to redness combines slowly with oxygen, forming red *cuprous oxide*, Cu_2O ,

and black *cupric oxide*, CuO . When the metal is exposed to the weather at ordinary temperatures, the surface slowly becomes covered with a green discoloration which has the composition indicated by the formula $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ and is identical with the mineral **malachite**.

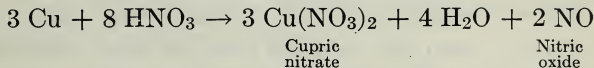
Copper is not dissolved by hydrochloric acid. Dilute sulphuric acid alone fails to affect it but in presence of oxygen slowly dissolves it to *cupric sulphate*:



Hot concentrated sulphuric acid rapidly converts it into cupric sulphate, with escape of sulphur dioxide:



Nitric acid, dilute or concentrated, dissolves it to a green solution of *cupric nitrate*, nitric oxide or nitrogen peroxide being given off:



Fine copper wire or thin sheet copper burns brilliantly in the vapor of sulphur to black *cuprous sulphide*, Cu_2S .

343. Uses. Copper is largely used for wires and cables for conducting the electric current. The electrical conductivity is seriously reduced by traces of impurities, which explains the fact that copper intended for the electrical industry is purified with special care. Copper is employed for roof gutters and cornices, for sheathing ships, and in making certain important alloys to be mentioned presently. Cooking utensils are often made of copper; because of the high conductivity of the metal for heat, they are economical of fuel, but they should be kept clean and bright, for copper compounds are poisonous, and if a

copper vessel becomes coated with a green deposit, dangerous quantities of copper may dissolve in the food that is prepared in it. To avoid this danger the interior of copper saucepans is often plated with tin, which is less easily tarnished and far less injurious.

The poisonous qualities of copper compounds find application in insecticides and fungicides for the farmer, such as Bordeaux mixture.

344. Electroplating. Steel is often plated with copper by a process called **electroplating**, the principle of which is the same as that of electrolytic refining. The object to be plated is placed in a solution of copper sulphate and made the cathode of a low-voltage direct current from a dynamo. The anode is a bar of pure copper.

This book is printed from copper plates made in a similar way. The text was set up in type, and the type made up into pages with engravings of the illustrations inserted at the proper places. An impression of each page was then taken on wax. This was coated with finely powdered graphite to make it conduct and then thinly electroplated with copper. The result was a hollow reproduction of the original type, which, owing to the graphite, was easily stripped from the wax. Melted lead with a little tin and antimony was then poured into the back of the electrotpe to strengthen it, making a plate about $\frac{1}{8}$ in. thick. Engravings of half-tone illustrations, which are engraved directly on copper, may be electrotyped as readily as type or line diagrams, or for added clearness in printing, the original engravers' plate may be incorporated in the electrotpe in the process of electroplating, as was done in the making of this book. Most books are now printed from **electrotpe** plates made in this way. Phonograph records are stamped in a plastic composition from a copper mould made by electrotyping the original record.

345. Alloys of copper. Copper is a constituent of a large number of useful **alloys**. **Brass** is made by melting copper in a

crucible and adding *zinc*. Most brasses contain about 2 parts of copper to 1 of zinc by weight. **Bronzes** are alloys of copper and *tin* in proportions which differ according to the purpose for which the alloy is to be used, as in the following examples:

	Per cent Copper	Per cent Tin	Per cent Lead
Bell metal.....	78	22	...
Gun metal.....	90	10	...
Coinage bronze.....	95	4	1

Statuary bronze is nearly the same as gun metal but contains also a little *zinc* and *lead*. **Phosphor bronze** contains, in addition to copper and tin, about 1 per cent of *phosphorus*, which adds materially to the hardness and strength of the alloy. The name **aluminum bronze** is given to the alloy of 90 per cent copper and 10 per cent *aluminum*. It has about the color and lustre of gold, is quite tenacious, and is scarcely affected by air and water. Aluminum bronze is used for cheap jewelry and for engineering purposes requiring strength combined with resistance to corrosion.

German silver is a brass whitened by the addition of *nickel*. It contains 60 per cent copper, 20 per cent zinc, and 20 per cent nickel. It is quite hard and strong and retains indefinitely its silvery lustre. The nickel coins of the United States are composed of an alloy of 75 per cent copper and 25 per cent nickel. The gold coins contain 10 per cent of copper, added to harden them and thus to reduce wear.

COMPOUNDS OF COPPER

346. Cuprous and cupric compounds. Copper forms two series of compounds, the *cuprous* and the *cupric*. In the **cuprous** compounds the copper atom is *univalent*, so that their formulas resemble those of the corresponding compounds of

sodium. *Cuprous oxide*, Cu_2O , occurs in nature as the mineral **cuprite**. Prepared artificially, it is a red powder, insoluble in water. When stirred with melted glass it dissolves, coloring the glass red. One kind of *ruby glass* is made in this way.

Cuprous sulphide, Cu_2S , is the mineral **chalcosite**. It can be obtained, as a black crystalline mass, by heating copper and sulphur together.

In the **cupric** compounds the copper atom is *bivalent*. Their formulas, therefore, resemble those of the corresponding compounds of *zinc*.

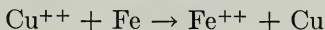
Cupric oxide, CuO , is often called "**black oxide of copper**." It is contained, along with cuprous oxide, in the scale that forms on copper when heated to redness in the air. Cupric oxide dissolves in melted glass, coloring the glass bluish-green, and is employed for this purpose. Its most important use is in the refining of certain kinds of petroleum found in Ohio and Texas, which have an offensive smell due to compounds of sulphur. The sulphur is removed and the oil deodorized by distilling the crude oil with cupric oxide.

347. Cupric sulphate, CuSO_4 . In the industries *cupric sulphate* is by far the most important compound of copper. It forms transparent blue crystals which dissolve in 3 times their weight of cold water and which have the formula $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. These crystals have long been known as **blue vitriol**, or **blue-stone**. Cupric sulphate is made by placing granulated copper in a perforated lead basket which is suspended over a tank containing warm dilute sulphuric acid. By means of a mechanical arrangement the basket is constantly dipped into the acid and lifted out of it again, and by the joint action of the sulphuric acid and the oxygen of the air the copper is slowly converted into a blue solution of cupric sulphate, which deposits in blue crystals upon strips of lead suspended in the tank when the liquid is allowed to cool. Much of the cupric sulphate of commerce is obtained as a by-product of the refining of silver bullion (§ 350).

Cupric sulphate is used in refining copper, in electroplating and electrotyping, in dyeing and calico printing, and in the preparation of insecticides and fungicides for the farmer. Wheat is steeped in a solution of cupric sulphate before sowing to prevent the development of "smut," a fungus which attacks the seed before it germinates. **Bordeaux mixture**, one of the most important sprays used by the agriculturist and fruit grower, is made by adding calcium hydroxide (slaked lime) to a cold solution of copper sulphate.

Reservoirs are sometimes suddenly invaded by microscopic water plants, which multiply rapidly and give the water an offensive odor and taste. The addition of 1 part of copper sulphate to 7,000,000 parts of water removes the trouble completely. The copper sulphate, placed in a canvas bag, is towed from the stern of a boat, which is rowed about the reservoir until the copper sulphate is all dissolved.

348. Tests for copper. A nail or a knife blade when immersed in a solution containing a salt of copper becomes plated with copper. An iron *atom* takes the electric charge from a cupric *ion* and converts it into metallic copper, while an iron *ion* is formed and dissolves in the liquid:



Ammonia added in excess to a solution of a *cupric* salt produces an intense blue color—a very delicate test. *Cuprous* salts remain colorless with ammonia, but the blue color appears when the liquid is shaken in contact with air.

SILVER (Ag = 108)

349. Occurrence. Native silver occurs in Mexico and Peru, in northern Ontario, and in Colorado, Arizona, and Montana, usually in slender filaments or thread-like forms. Nuggets weighing several hundred pounds have been found. The native copper of the Michigan mines is often rich in silver.

Most ores of *lead* contain silver, and the crude lead made from such ores generally carries enough silver to pay for its extraction. In the United States much of the silver of commerce is obtained from this source.

Some important ores of silver are the following:

ORES OF SILVER

Scientific Name	Miner's Name	Formula	Color
CERARGYRITE.	Horn silver	AgCl	Gray, turning black on exposure to light
ARGENTITE . . .	Silver glance	Ag_2S	Blackish gray
PROUSTITE . . .	Light-red silver ore	Ag_3AsS_3	Scarlet
PYRARGYRITE.	Dark-red silver ore	Ag_3SbS_3	Blackish red

350. Extraction. The extraction of silver from crude lead is so convenient that in this country silver ores are often mixed with lead ores and the two smelted together. Lead containing silver results, from which the silver is recovered.

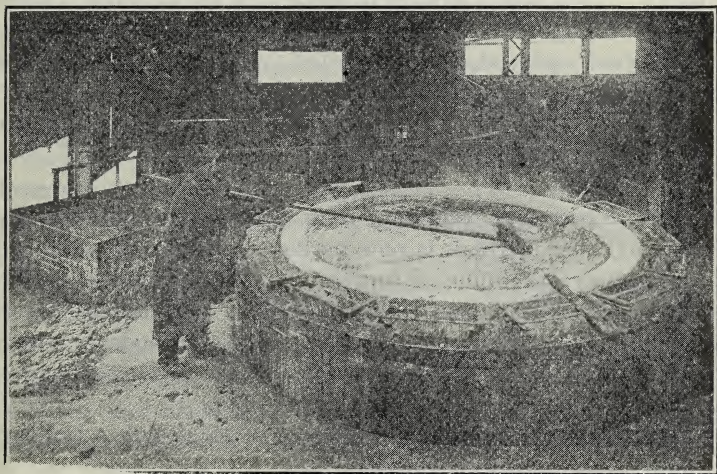
In order to accomplish this the lead rich in silver is melted in an iron kettle holding 30 tons, and 1 per cent of zinc is stirred into it. On standing a scum rises and solidifies to a crust, which is removed. This crust contains, along with zinc and lead, all of the gold and silver present in the ores used.

The removal of the *zinc* from the alloy thus obtained is based on the fact that zinc is converted into vapor at a far lower temperature than lead, silver, or gold. The alloy is heated in a closed retort; the zinc distills away and is condensed and used again.

The alloy of lead, silver, and gold is removed from the retort, melted in an iron pot, and run into a shallow depression in a furnace the hearth of which is lined with bone ash. Here it is heated by a flame which plays on the surface of the metal, while at the same time a blast of air is introduced. Gold and

silver, being noble metals, are not oxidized by this treatment, but lead is converted into *lead oxide*, PbO , which flows off through a notch in the rim into an iron pot.

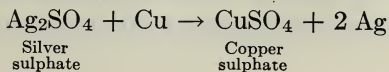
As the last traces of lead are removed, brilliant rainbow hues appear on the melted mass, and finally the bright surface of the silver breaks through the lead oxide with a flash. Then the blast is stopped and the metal cast into ingots which consist of silver and gold with traces of copper and iron.



Courtesy of the National Lead Co.

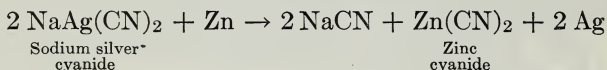
Fig. 188. Desilverizing lead.

When this alloy is heated with concentrated sulphuric acid and then warmed with water, the gold, which is not affected by the acid, remains as a brown "mud," while the sulphates of silver, copper, and iron dissolve. When plates of pure copper are hung in this solution, silver deposits upon them in beautiful crystals, while copper sulphate dissolves:



The pure silver is melted into bars. The liquid, when evaporated and cooled, deposits blue crystals of *cupric sulphate*, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. This is the source of much of the cupric sulphate of commerce.

351. The cyanide process. Ores containing horn silver, AgCl , or silver glance, Ag_2S , are often treated by the **cyanide process**, which consists in agitating the powdered ore in a large wooden tank with a 1 per cent solution of sodium cyanide, NaCN . The silver slowly dissolves to form *sodium silver cyanide*, $\text{NaAg}(\text{CN})_2$. The solution is filtered to get rid of the undissolved material, and in another vessel zinc dust is added to the clear liquid to precipitate the silver:



352. Electrolytic refining. The crude silver obtained by this and other methods is now purified by a process similar to the electrolytic refining of copper. The liquid used is a solution of silver nitrate containing nitric acid. The impure silver, cast into plates, forms the anode, and the cathode is a thin plate of pure silver. Refined silver deposits at the cathode in crystals, which are melted and cast into bars.

353. Physical properties. Silver is a metal with a brilliant white lustre, which is familiar from the widespread use of mirrors made by depositing a film of silver on glass. Its specific gravity is 10.5, and it is, therefore, a little lighter than lead. It is softer than copper, but rather harder than gold. In malleability it is surpassed only by gold, and in ductility only by gold and platinum. Of all substances silver is the best conductor of electricity and of heat. It melts at 960° .

354. Chemical conduct. Since oxygen has no action upon it, silver retains its lustre when heated in the air. Molten silver absorbs 22 times its volume of oxygen, but the oxygen is merely dissolved and is expelled with energy when the metal solidifies.

Sulphur combines rapidly with silver when heated, and slowly in the cold, converting it into black *silver sulphide*, Ag_2S . This is the explanation of the darkening of silver coins when carried in the pocket with pencil rubbers or rubber bands. The rubber contains sulphur, which darkens the surface of the coin by converting it into silver sulphide. Eggs and mustard both contain sulphur compounds and therefore rapidly darken silver spoons.

Oxidized silver is a name given to silver the surface of which has been covered with a thin layer of silver sulphide. This is done by immersing the object in a solution of potassium sulphide. The *tarnish* which develops upon the silverware of the household is a film of silver sulphide. It results from the action of traces of hydrogen sulphide which appear in the air when coal is burned.

Silver is but slightly affected by hydrochloric acid or dilute sulphuric acid. Concentrated sulphuric acid converts it into silver sulphate, and nitric acid, even when dilute dissolves it, forming silver nitrate:

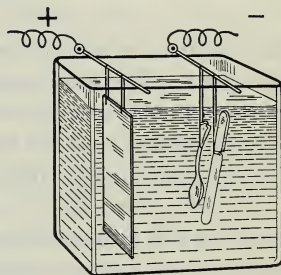
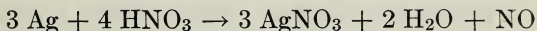


Fig. 189. Silver plating.



Silver surpasses platinum in resistance to the action of alkalies like sodium hydroxide and potassium hydroxide, and silver vessels are employed in the laboratory when it is necessary to melt these substances.

355. Uses. Silver is so soft that it would wear away rapidly in use, and it is always hardened by alloying it with a small proportion of copper. The silver coins of the United States and of most other countries contain 90 per cent of silver

and 10 per cent of copper. The English silver coins, however, contain 92.5 per cent of silver and 7.5 per cent of copper. This mixture is called **sterling silver** and is the alloy used in the manufacture of articles of "solid silver."

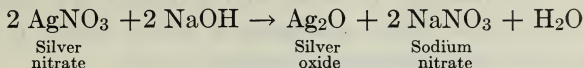
Silver plating (Fig. 189) resembles the process of copper plating (§ 344). The liquid is a water solution of the double cyanide of silver and sodium, $\text{NaAg}(\text{CN})_2$, and the anodes are plates of pure silver. The object to be plated, which is made of a white alloy like German silver and which must be most carefully cleaned, is made the cathode. The voltage across the cell is very low. Silver dissolves from the anode at the same rate as it deposits on the cathode, so that the total quantity of silver dissolved in the bath remains the same. The silver coating is dull white. The high lustre of commercial silverware is due to subsequent polishing. In cleaning silver-plated ware it should be remembered that the surface is pure silver and is softer and more liable to injury than the surface of solid silver articles.

A **mirror** consists of a polished piece of plate glass on the back of which a film of silver has been deposited. The following is a simple way of accomplishing this. Dissolve 1 gram of silver nitrate in 100 c.c. of distilled water and add ammonia drop by drop, with constant stirring, until the precipitate which first forms has *almost* disappeared. Now add 0.5 gram of potassium hydroxide dissolved in water, and continue adding ammonia until the liquid is clear. This fluid, which must be made up at the time it is required, is placed in a *perfectly clean* beaker, a few drops of glycerine added, and a gentle heat applied. The interior of the vessel rapidly becomes coated with a lustrous film of silver, which can easily be removed after the experiment by rinsing out the beaker with a few drops of nitric acid.

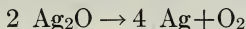
COMPOUNDS OF SILVER

356. Silver oxide, Ag_2O . Unlike the "base metals," silver does not oxidize when heated in the air. Silver oxide is

obtained by adding sodium-hydroxide solution to a solution of silver nitrate:



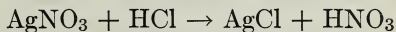
Silver oxide is a brown powder, almost insoluble in water. When dry silver oxide is heated, oxygen escapes, and a residue of silver remains:



357. Silver sulphide, Ag_2S . Silver sulphide is found in Mexico and Peru and in Nevada, Arizona, and Michigan as the blackish-gray mineral **argentite** or *silver glance*, which is a silver ore of some importance. The fact that it can be easily cut into chips with a knife distinguishes argentite from other minerals of similar appearance.

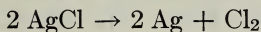
358. Silver chloride, AgCl . Silver chloride is found in the silver mines of Peru, Chile, and Mexico as the gray mineral **cerargyrite** or *horn silver*, which turns black on exposure to light.

In the laboratory silver chloride is obtained, as a white, curdy precipitate by adding hydrochloric acid, or a solution of a chloride, to a solution of silver nitrate:

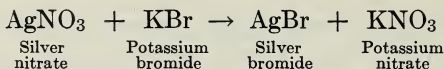


We have already discussed the use of this chemical change as a test for *chlorine ions*. In a similar way the addition of hydrochloric acid serves as a test for *silver ions* in a solution.

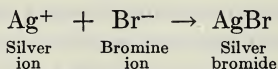
Silver chloride is a white solid, insoluble in water but freely soluble in ammonia. When exposed to light it turns first violet and then black. This change in color is due to the formation of metallic silver, with escape of chlorine:



359. Silver bromide, AgBr. Silver bromide is occasionally found as a bright-yellow mineral in Mexican and Chilean silver mines. It is insoluble in water, and is formed as a yellowish-white precipitate, when a solution of silver nitrate is mixed with a solution of potassium bromide:

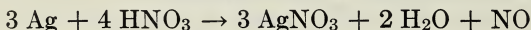


Since the combination is only between the silver ions and the bromine ions, any soluble silver salt and any soluble bromide will give the same result:



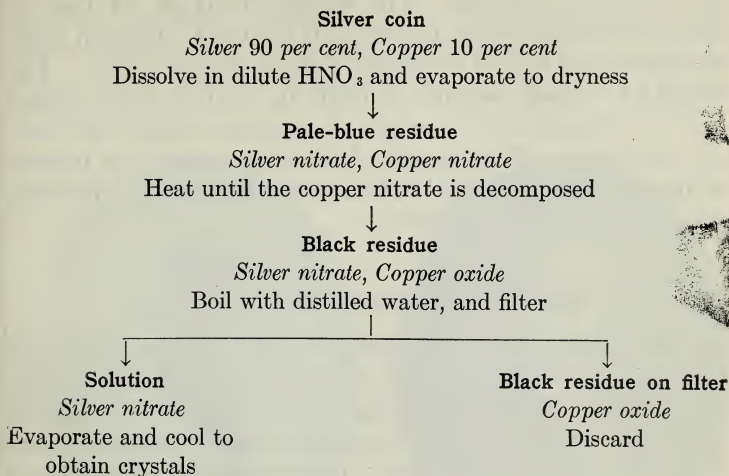
Like silver chloride, silver bromide is slowly decomposed by light, bromine escaping, while a dark residue of silver remains. This behavior is the basis of **photography** and will be further discussed in connection with that subject.

360. Silver nitrate, AgNO₃. Silver nitrate is prepared by dissolving silver in nitric acid and evaporating the solution until, when cooled, it deposits crystals:



Sterling silver and coin silver contain copper and when dissolved in nitric acid yield a blue solution containing both silver nitrate and copper nitrate. It is easy, however, to prepare pure silver nitrate from such a solution by evaporating it to dryness in a dish and gently heating the blue residue until it becomes black. This blackening is due to the conversion of the copper nitrate into copper oxide, which is *insoluble in water*. The silver nitrate is not affected. When the heated residue is warmed with water and filtered, a black powder of copper oxide remains upon the filter. The colorless liquid which runs

through the filter is a pure solution of silver nitrate, from which marketable crystals can be obtained by evaporation followed by cooling. A diagram will make the process clear:



Silver nitrate forms colorless, square tabular crystals, which dissolve in less than half their weight of water at room temperature ($20^\circ \text{C}.$). This free solubility in water is of great importance in the practical applications of silver nitrate. Most of the other silver salts are either insoluble or not sufficiently soluble to permit of their use in industrial and scientific work.

A spot of silver-nitrate solution placed upon paper becomes black when exposed to sunlight. This is because the silver nitrate, under the influence of light, yields its oxygen to the paper fibre and is itself reduced to finely divided silver, which appears as a black deposit. For the same reason silver-nitrate solution produces black spots upon the hands. The discoloration can be removed by the careful application of tincture of iodine, followed by ammonia.

Silver nitrate is by far the most important compound of the

metal. Its chief market is in the photographic industry, where it is employed in the manufacture of films, plates, and paper. It is used in making mirrors and in silvering glass for optical and decorative purposes. The indelible marking ink used in laundries contains silver nitrate, and the mark produced upon the garment is due to a deposit of finely divided silver. The druggist's "**lunar caustic**" is made by melting silver nitrate with one-twentieth of its weight of potassium nitrate and casting into sticks. The removal of warts by caustic is a process of gradual oxidation; the blackening which is always noticeable is caused by a deposit of silver.

PHOTOGRAPHY

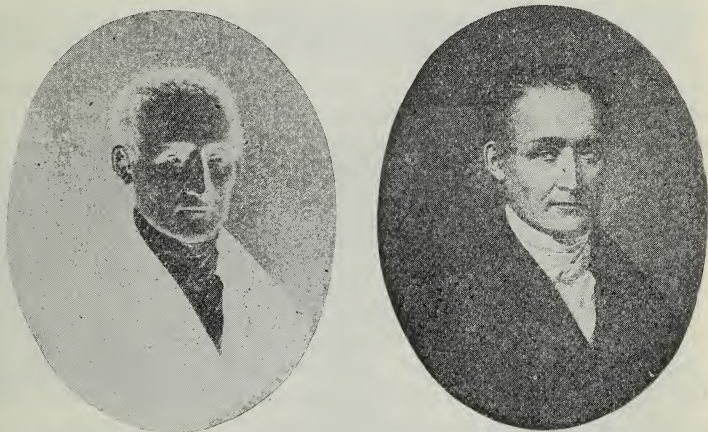
361. Exposure. A photographic film is a thin sheet of transparent celluloid, one side of which is covered with a layer of hardened gelatin containing *silver bromide*. The film is placed in the camera in such a position that the sensitive surface is in the focus of the lens. Light is admitted through the lens by an ingenious shutter. The **exposure** is usually very brief, averaging, in direct sunlight, one-thirtieth of a second.

362. Development. The action of light for such a brief time produces *no visible effect* upon the silver bromide. It is only when the film is **developed** that an image appears.

A developer is a substance that will convert silver bromide into dark, finely divided silver *provided that the silver bromide has been exposed to light*. Upon silver bromide that has always been protected since its formation developers have little or no action. During development, therefore, those parts of the film that correspond to the bright portions of the original scene—such as the sky—turn dark, whereas the parts of the film that correspond to the darker portions of the original remain light, because here the silver bromide is unaffected.

363. Fixing. The next step is to remove the unchanged silver bromide from the film, for it would otherwise turn black

when exposed to light and destroy the image. This process is called **fixing**, because it makes the image permanent. It is accomplished by soaking the film in a solution of *sodium thio-sulphate*, $\text{Na}_2\text{S}_2\text{O}_3$, called "**hypo**" by the photographer. This solution dissolves silver bromide readily, and when the film has been soaked in it for 20 minutes, it can be freely exposed to light without injury.



Courtesy of the "Scientific American."

Fig. 190. Negative and positive of photograph.

The subject is Joseph Nicéphore Niepce (1765-1833), French chemist, who first obtained permanent pictures by the action of light on chemicals.

After being washed and dried, the film is ready for *printing*. It is now called a **negative** for the lights and shadows of the original scene are reversed in it.

All that has been said of films applies equally to photographic plates, except that in plates the foundation is *glass* instead of celluloid.

364. Printing. In printing the negative is placed in a frame and exposed to light with a piece of sensitized paper back of it in contact with the sensitized side of the film. The

light passes easily through the clear portions, which therefore become dark when the print is developed, but is arrested by those parts which are covered with opaque silver, which therefore remain white on the paper. Hence the lights and shadows are again reversed and with careful work can be made to correspond to those of the original subject.

Many different varieties of papers are employed for printing. For most amateur and professional work the simplest and most satisfactory are the "developing papers," like "Velox" and "Cyko," which work on the same principle as a film. The sensitive layer is composed of gelatin containing silver bromide or silver chloride. When exposed back of a negative the paper remains white, but the picture appears upon dipping the paper into the developer. Fixing is accomplished in the same way as with a film, by soaking the print in a solution of sodium thiosulphate, washing, and drying.

GOLD (Au = 197)

365. Occurrence. Gold is found almost entirely *native*. The deposits are of two different varieties, both of which are of great importance as sources of the metal:

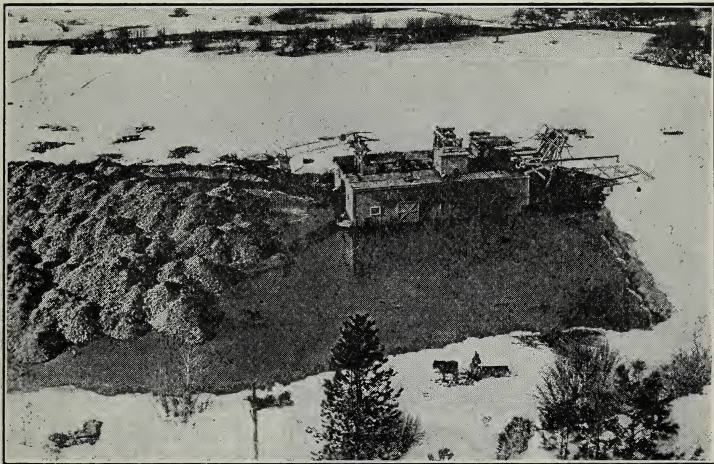
1. **Placer deposits** contain the gold in the form of dust, scales, or nuggets, disseminated through the sand or gravel of river valleys.

2. **Gold reefs** are veins of quartz of volcanic origin, which occur intersecting slaty rocks of a dull gray or greenish color. The gold can often be seen scattered through the quartz in shining yellow scales, but frequently it is so finely divided as to be invisible. The mineral *pyrite*, FeS_2 , usually occurs with the gold, and near the surface the gold quartz is honey-combed and iron-stained by the decomposition of the pyrite under the influence of the weather.

Gold occurs in South Africa, in Australia, in British Columbia, in the United States, especially in Alaska, California, Utah,

and Idaho, and in many other localities. One-fifth of the total annual production of gold is obtained in the United States.

366. Extraction. *Placer deposits* are usually worked by *washing* the gravel in devices which remove the greater part of the lighter barren rock grains, followed by treatment of the *concentrate* by the cyanide process. The sandy concentrate is digested in a large tank with a solution of sodium cyanide,



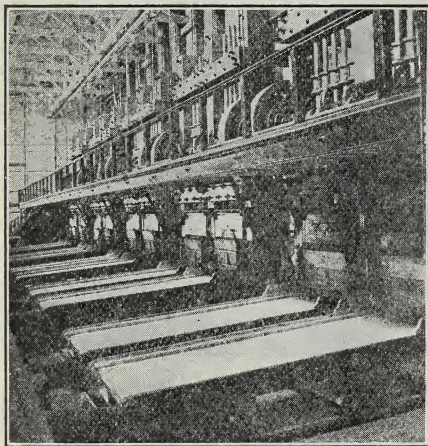
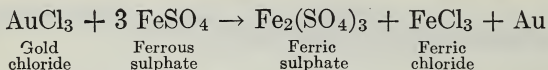
Courtesy of the Bureau of Mines.

Fig. 191. Dredging placer gravels for gold in Idaho; gold dredges are floating concentrators.

which dissolves the gold. The clear solution is drawn off into another vessel, and the gold precipitated by adding zinc.

The rock of a *quartz vein* is broken in a crusher and then pounded to powder in a *stamp mill*, in which the broken quartz is placed in a strong iron receptacle, and a heavy weight is allowed repeatedly to fall upon it. The powdered quartz, mixed to a cream with water, flows out over inclined copper plates smeared with mercury, which alloys with and detains a portion of the gold, which is recovered by distilling off the

mercury. The balance of the gold is extracted from the powdered quartz by the cyanide process or by treatment with chlorine and water. In the latter "*chlorination*" process the gold is converted into gold chloride, AuCl_3 , which dissolves. The liquid is filtered, and from the clear solution the gold can be precipitated by adding a solution of ferrous sulphate, FeSO_4 , or in other ways:



Copyright, Keystone View Co.

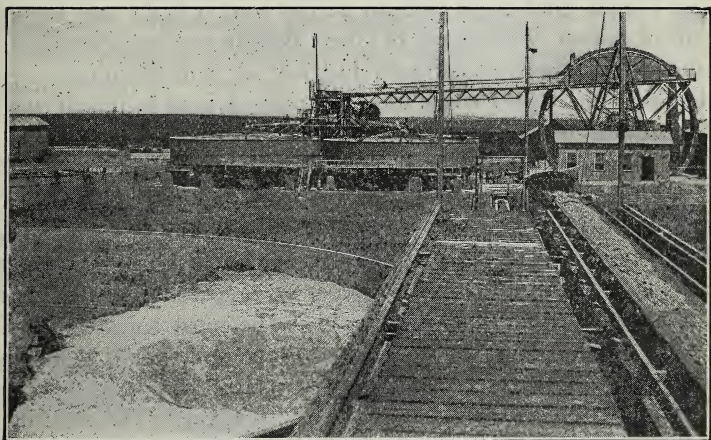
Fig. 192. Gold stamp mills and amalgamation plates.

In any case the crude, spongy gold obtained is melted into bars, and sold as "bullion," which contains silver, copper, iron, and traces of other metals. The separation of silver from gold by means of sulphuric acid and the electrolytic refining of copper rich in silver have already been described. Gold bullion is refined in the Mint by an electrolytic process similar to the re-

fining of copper. The bullion is the anode, the cathode being a thin plate of pure gold and the liquid a solution containing gold chloride and hydrochloric acid.

367. Physical properties. Gold is a yellow metal a little softer than silver and nearly twice as dense (sp. gr. 19.3). It is the most ductile and malleable of the metals. One gram of

gold can be drawn into a wire 3 kilometers long (half an hour's brisk walk). A skilled workman can beat the metal into leaf only $\frac{1}{10,000}$ of a millimeter thick. It would take 250,000 such leaves in contact to make a pile 1 in. in height. Each leaf is so thin that it transmits a green light. Gold is a good conductor of electricity and of heat, but its specific heat is low,



Photograph from Ewing Galloway.

Fig. 193. A South African cyanide plant; spent sand is being removed from the tank in the foreground.

and hence a gold coin feels warmer to the hand than does a copper or silver coin at the same temperature.

Gold melts at $1,094^{\circ}$ and has therefore almost the same melting point as copper. It boils at $2,500^{\circ}$.

368. Chemical conduct. Gold is an inactive element. Compared with the base metals, it forms few compounds, and they are all easily decomposed by heat, leaving a residue of gold. The affinity of gold for oxygen is feeble, and therefore the metal retains its lustre in the air even at a red heat and is not affected by water at any temperature.

Gold is not acted on by the three common acids singly, but aqua regia dissolves it to a solution of *gold chloride*, AuCl_3 . Chlorine water slowly produces the same effect, and tincture of iodine will convert the metal into gold iodide if time enough be given.

369. Uses. Gold is so soft that for use it is alloyed with copper or with copper and silver to harden it. The American and French gold coins contain 90 per cent of gold and 10 per cent of copper, while those of Great Britain are composed of an alloy of 92.5 per cent of gold and 7.5 per cent of copper. In the Australian gold coins 92.5 per cent of gold is mixed with 7.5 per cent of silver.

The jeweler expresses the purity of his gold in "carats." A carat is one twenty-fourth part. Pure gold is 24 carats fine. The British coins are 22-carat, and the American 21.6-carat. The 18-carat gold which is in use for rings is $\frac{18}{24}$, or 75 per cent, gold, the balance being copper or copper and silver. For most other purposes 14-carat gold is the most suitable alloy. This is hard enough to stand wear quite well, but it contains sufficient gold to protect it against tarnish (58.33 per cent).

Gold plating is similar to plating with silver. The carefully cleaned object is made the cathode in a solution of the double cyanide of gold and sodium, $\text{NaAu}(\text{CN})_2$. The anode is a plate of pure gold which dissolves as gold is deposited at the cathode, keeping the percentage of gold in the liquid the same. Among the minor uses of gold are its employment for painting on china, for the preparation of gold leaf, and in dentistry.

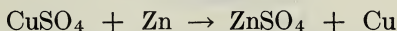
370. The touchstone. The fact that gold is not affected by nitric acid serves to distinguish it from brass and other yellow alloys that resemble it in appearance. However, plated articles resist nitric acid just as well as solid gold does. The jeweler, who is constantly obliged to value "old gold" with a view to purchase, works with a set of standard needles which are 8-carat, 10-carat, 12-carat, 14-carat, etc., fine and a slab of black stone (basalt) called a *touchstone*. Over this he draws the

metal to be investigated, which leaves a shining streak, and for comparison he makes streaks on the stone with his standard alloys. By comparing the behavior of these streaks with nitric acid he can ascertain in a short time the fineness of the alloy offered.

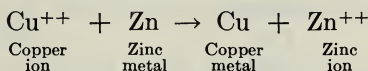
371. Auric chloride, AuCl_3 . Auric chloride, the most important compound of gold, is made by dissolving gold in aqua regia, evaporating, and drying the residue at 120° ; auric chloride remains in reddish-brown crystals, which are used in photography in "toning" prints.

THE ELECTROMOTIVE SERIES OF THE METALS

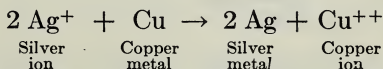
372. When a strip of zinc is placed in a solution of copper sulphate or any other soluble copper salt, a red deposit of *copper* is produced upon the zinc. At the same time zinc dissolves:



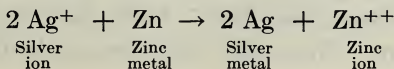
or, better:



A strip of *silver*, however, is *not* coated with copper when dipped into a solution containing copper ions. On the contrary, when copper is placed in a solution containing silver ions, *silver* is deposited upon the copper. Since silver is univalent, the equation is:



Zinc placed in a solution containing silver ions becomes coated with *silver*:



Hence, if we arrange these three metals in the following order:

Zinc
Copper
Silver

we may say that each metal *precipitates* those that follow it, and *is precipitated* by those that precede it. When all of the important metals are included in an investigation of this sort, the resulting arrangement is known as the **electromotive series**. It is as follows:

The Sodium Group
The Calcium Group
Magnesium
Aluminum
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
HYDROGEN
Copper
Antimony
Bismuth
Mercury
Silver
Platinum
Gold

Any metal in this series will precipitate *metal* from a solution containing *ions* of any of the metals that follow it, but will not affect a solution containing ions of a metal preceding it. The metals preceding *hydrogen* liberate hydrogen gas from solutions containing hydrogen ions, that is from *acids*; those that follow hydrogen do not. Since *water itself* contains hydrogen ions, the

metals preceding hydrogen *rust* in contact with water; for this reason they are hardly found in the free state in nature. Those following hydrogen scarcely rust and are therefore found native, although most of them also occur as compounds. The student will note that chemical activity decreases as we descend the table, the sodium group being intensely active, while platinum and gold are the most inert of the metals.

Galvanized iron resists the action of the weather much better than iron plated with tin. The electromotive series explains this fact. Since zinc precedes iron, water will have no action upon the iron until the zinc has all rusted. On the other hand, since iron precedes tin, the iron rusts first when iron and tin are exposed together to water. Hence the protection afforded by tin against rusting lasts only as long as the plating of tin over the iron remains unperforated.

SUMMARY

Native copper is found in northern Michigan. Ores containing copper, iron, and sulphur occur abundantly in Montana, Arizona, and Utah.

Copper is a red metal which is only about half as tough as iron and rusts far more slowly. It is employed for purposes in which resistance to corrosion is more important than strength. Its largest use is in the electrical industry.

The chief alloys of copper are **brass**, which is composed of copper and zinc, and **bronze**, which contains copper and tin.

The most important compound of copper is **cupric sulphate**, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, often called **blue vitriol** or **bluestone**.

Silver is obtained chiefly in South America, Mexico, and the United States. Much of the silver obtained in the United States is recovered from crude lead by treatment with zinc.

Silver is harder than gold and nearly as dense as lead. It is the best conductor of electricity and heat. It does not oxidize in the air. The *tarnish* which appears on its surface is a film of silver sulphide.

Silver nitrate, AgNO_3 , is used in the manufacture of photographic supplies and in making mirrors.

Photography depends upon the fact that silver bromide that has been exposed to light is converted into black, finely divided silver by the developer, whereas unexposed silver bromide remains unaffected during development.

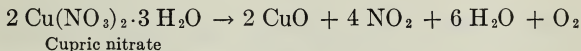
Gold occurs chiefly native. It is extracted by the cyanide process or by treating the ores with chlorine and water. For jewelry and coinage gold is alloyed with copper or silver.

The **electromotive series** contains the metals so arranged that a metal is precipitated from a water solution of a compound by a metal standing before it in the series but not by one following it.

EXERCISES

1. How could you prove the presence of copper and silver in a ten-cent piece?
2. Copper, silver, and gold were known and used long before iron. Why?
3. Why are there so many ancient weapons of copper and bronze in museums and so few of iron?
4. Which would be the better, copper or iron, for a bridge truss? For a rail? For the cornice of a dwelling? For a roof gutter? For fly screens? Why?
5. In market reports price quotations are given for "Lake copper" and for "electrolytic copper." What is the distinction?
6. How does *sterling silver* differ from *coin silver*?
7. What is a *developer*? What is the purpose of the "hypo"? Why are photographic films and prints washed thoroughly after they are "fixed"?
8. How is the electric current applied in the purification of copper, silver, and gold?
9. How could you ascertain whether a ring was solid gold or merely plated?
10. What would be the result of wearing a silver chain in a laboratory in which hydrogen sulphide was being used?

11. Why are the elements preceding hydrogen in the electromotive series not found free in nature?
12. A strip of silver in a solution of auric chloride becomes coated with gold. Write the equation.
13. Compare the copper family with the sodium family.
14. How is copper extracted from its ores?
15. Describe the extraction of silver from crude lead.
16. What is the cyanide process?
17. How many grams of potassium bromide and how many of silver nitrate are needed to prepare 12 grams of silver bromide?
18. Two grams of powdered copper were heated in oxygen. 2.5063 grams of cupric oxide, CuO , were produced. Calculate the atomic weight of copper if that of oxygen is taken as 16.
19. I require 120 grams of cupric oxide. How many grams of crystallized cupric nitrate must be heated to redness in order to make it?



20. Calculate the percentage composition (a) of silver chloride, AgCl ; (b) of silver sulphide, Ag_2S ; (c) of silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$.
21. How many grams of zinc are required to precipitate 5 grams of silver from solution?
22. 1.4 grams of an alloy of copper and silver was dissolved in dilute nitric acid, and hydrochloric acid added. The silver chloride that was precipitated weighed 1.6 grams. How many grams of silver and copper were present and what was the percentage composition of the alloy?
23. What percentages of copper, carbon, hydrogen, and oxygen are contained in the green rust that forms on copper exposed to the weather?
24. How many grams of silver nitrate can be obtained by dissolving 100 grams of United States silver coins in nitric acid and treating as described in section 360? How many grams of silver nitrate can be obtained by treating 100 grams of British silver coins in the same way?

25. 98.5 grams of gold are dissolved in aqua regia, evaporated, and the residue heated to 120° . Required, the name, formula, and weight of the residue.

REVIEW QUESTIONS

1. Why does a solution of copper sulphate redden blue litmus paper?

2. Why is a solution of sodium carbonate alkaline to litmus?

3. Compare the action of dilute sulphuric acid on zinc with that of concentrated sulphuric acid on copper. Does the position of the two metals in the electromotive series throw any light upon the cause of the difference?

CHAPTER XXXI

GROUP II A. THE CALCIUM FAMILY

CALCIUM, STRONTIUM, BARIUM, RADIUM

373. General. The members of the Calcium Family are typical *light* metals, which possess the metallic lustre, but show little malleability, ductility, or tenacity, and occur in nature only in their compounds. Like the metals of the Sodium Family, they burn brilliantly to their oxides when heated in the air, and are rapidly converted into their hydroxides by water with escape of hydrogen. The metals of the calcium family are *bivalent*.

Calcium is by far the most abundant metal of the group. *Strontium* and *barium* are less important and will be only briefly discussed. *Radium*, though very rare, is, in some respects, the most remarkable of all of the elements. It will be studied in detail in the final chapter.

CALCIUM (Ca = 40)

374. Occurrence. The compounds of calcium are so widespread in nature that it stands fifth among the elements in order of abundance, making up 3.42 per cent of the crust of the earth. Some of the important calcium minerals are listed in the table on the next page.

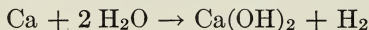
375. Preparation. Calcium is obtained by the electrolysis of melted *calcium chloride* in a graphite crucible which forms the anode. Here chlorine gas escapes. The calcium attaches itself to the cathode, which is an iron rod dipping into the liquid. As the calcium accumulates, this rod is raised by a

IMPORTANT CALCIUM MINERALS

	Calcium Carbonate CaCO_3	Calcium Sulphate $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	Calcium Fluoride CaF_2	Calcium Phosphate $\text{Ca}_3(\text{PO}_4)_2$
MINERALOGICAL NAME.	Calcite	Selenite	Fluorite	Phosphorite
FAMILIAR NAME.....	Limestone, marble, etc.	Gypsum	Fluor spar	Phosphate rock
CRYSTAL FORM.....	Rhombohedron (Fig. 194)	Prismatic, tabular (Fig. 203)	Cubic (Fig. 203)	Amorphous
COLOR.....	Colorless when pure	Colorless	Violet, green, yellow, etc.	Grayish white
USES.....	See text	Making plaster, fertilizer	Flux, making hydrofluoric acid	Fertilizer manufacture

screw, so that the calcium itself becomes the cathode, and a lengthening stick of it is formed.

376. Properties. Pure calcium is silver-white, but the commercial metal is gray. It is about as hard as aluminum. Its specific gravity is 1.5, and it melts at 810° . Heated in the air, it burns brilliantly to *calcium oxide*, CaO . When thrown into water, calcium gives off hydrogen and is converted into a white powder of *calcium hydroxide*, $\text{Ca}(\text{OH})_2$:



Calcium is a very active metal, and when heated it combines rapidly with chlorine, sulphur, nitrogen, and many other elements, often with combustion. Calcium compounds give an *orange* color to the Bunsen flame.

Thus far calcium has found no industrial applications. It is employed in school laboratories for showing the liberation of hydrogen from water, for which purpose it has the great advantage over sodium that the experiment is free from danger.

377. Calcium in the diet. The bones and teeth are largely composed of calcium compounds, and from this it follows that a regular supply of calcium in the food is essential to the proper

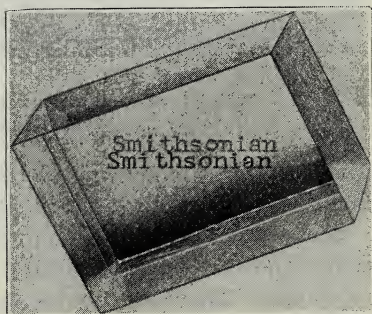
nutrition of the body. This is especially true of children, in whom the bony skeleton is growing rapidly. On the average each person's food should contain at least 0.75 gram of calcium per day. It is likely that in American families there is more often a deficiency of calcium in the diet than of any other necessary element.

Meats are poor in calcium. Eggs, cereals, and vegetables contain larger percentages. Among foods rich in calcium are peas, beans, cheese, and especially milk. A glass of milk contains a little more calcium than the same volume of pure saturated limewater. Professor Sherman says: "By far the most practical means of insuring an abundance of calcium in the dietary is to use milk freely as a food." The calcium in food products occurs only in the form of compounds, some of which are highly complex.

CALCIUM CARBONATE, CaCO_3

378. Occurrence. Calcium carbonate, or **calcite**, is found in transparent colorless crystals which often have the form of a rhombohedron such as that shown in Figure 194. The same figure illustrates the remarkable power of the crystal to separate light into two rays which take different directions, so that objects seen through it appear double. This property, called **double refraction**, is utilized in optical apparatus.

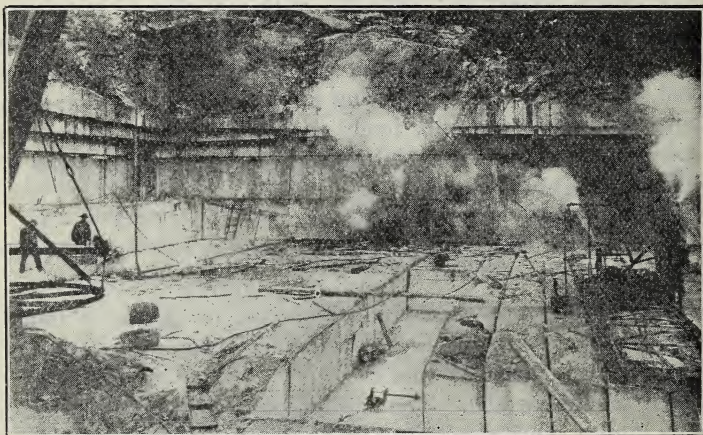
Marble is a mass of minute crystals of calcium carbonate. The sparkling appearance of freshly broken marble is due to the reflection



Courtesy of the U. S. National Museum.

Fig. 194. Calcite crystal showing double refraction.

of light from the surfaces of the crystals, but they are so crowded together that no crystal has had space to develop its perfect form, the structure being similar to that of a cube of table sugar. Marble is white when pure, but it is often beautifully veined and colored by traces of impurities. The uses of marble for sculpture, for ornamental objects like table tops, and as a building stone are familiar. The fragments discarded from these operations are made into *lime*. Marble dust with



Courtesy of the U. S. Geological Survey.

Fig. 195. Cutting dimensioned blocks from an Alaska marble quarry with a channeling machine.

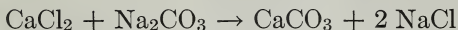
sulphuric acid is employed to generate carbon dioxide for the production of soda water and other carbonated drinks.

Limestone is chiefly calcium carbonate, but it also contains magnesium carbonate (MgCO_3), silica (SiO_2), clay, and other impurities. The color varies greatly in different specimens but is often bluish gray. As a rule no crystal faces are visible on the fracture. **Chalk** is a soft, white limestone which is composed of microscopic shells. **Coquina**, found in Florida, is a limestone formed of larger shells cemented together. In fact,

most shells are composed chiefly of calcium carbonate, and the same statement is true of coral and of the pearl. Limestone is used as a building stone and in road making. Broken limestone serves as a foundation for asphalt paving. *Concrete* is often made by mixing small fragments of limestone with cement and water. Millions of tons of limestone are consumed annually in the production of iron in the blast furnace. Pure white limestone forms an important raw material of the glass industry. Large quantities of limestone are "burned" for the manufacture of *lime*.

An *acid* soil is one which, when allowed to remain in contact with moist blue litmus paper, changes the color to red. Acid soils give poor results with most crops. Powdered limestone applied in quantities of a ton per acre every five years neutralizes the acid in such soils and greatly improves their properties. Soils containing a high percentage of *clay* are stiff and difficult to work. They often become mellow and tillable after an addition of powdered limestone.

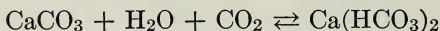
379. Preparation. Calcium carbonate made artificially is sold as a fine white powder under the name **precipitated chalk** or **whiting**. It is prepared by adding a solution of sodium carbonate to one of calcium chloride:



The white precipitate of calcium carbonate is allowed to settle, and the solution of sodium chloride drawn off and discarded. The calcium carbonate is then stirred up with water and again allowed to settle, in order to wash it; this is repeated several times, after which the product is dried and pulverized for use.

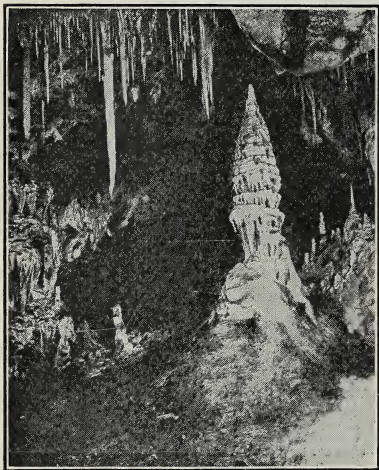
Calcium carbonate made in this way is used as a dentrifice, as a polishing powder, as a pigment, and as a "filler" for rubber and paper. Mixed with one-sixth of its weight of linseed oil, it forms **putty**.

380. Solubility. As everyday experience with marble shows, calcium carbonate is almost insoluble in water. However, if the water contains dissolved carbon dioxide, calcium carbonate becomes soluble in it. The reason is that *calcium hydrogen carbonate*, $\text{Ca}(\text{HCO}_3)_2$, is formed, which is 30 times as soluble in water as is calcium carbonate itself:



If the carbon dioxide is driven out by boiling the water or by exposing it to the air, the above equation is reversed, and calcium carbonate is deposited.

The soil water is rich in carbon dioxide. Hence it has a marked solvent action on calcium carbonate, so that when the soil water filters through a layer of limestone, the rock is slowly dissolved and removed. The Luray Caverns, the Mammoth Cave, and many similar caverns found in limestone rock are the result of this process.



Courtesy of the Philadelphia Commercial Museum.

Fig. 196. Stalactites and stalagmites.

A **stalactite** is a mass of calcium carbonate hanging like an icicle from the roof of a cave. The water, charged with calcium hydrogen carbonate, as it drips from the roof, gives off carbon dioxide into the air and deposits calcium carbonate, forming the stalactite. Where the drop strikes the floor, more calcium carbonate deposits, and a rounded mass called the **stalagmite**.

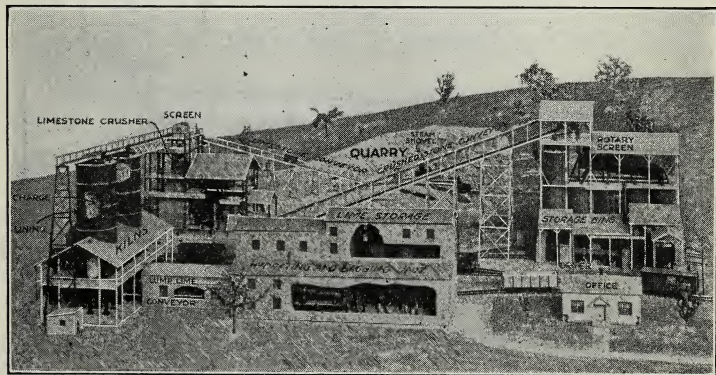
grows up until the two unite and form a column. Eventually, the cavern may be filled up again in this way.

CALCIUM OXIDE, CaO

381. Preparation. Calcium oxide, commonly called **lime**, is made by heating calcium carbonate to a white heat, with liberation of carbon dioxide:



As the arrows indicate, the change is reversible. Hence, when calcium carbonate is heated in a closed vessel, the carbon



Courtesy of the National Lime Association.

Fig. 197. A modern lime plant using shaft kilns.

dioxide that accumulates begins to unite again with the lime to form calcium carbonate. When this recombination balances the decomposition of the calcium carbonate, **chemical equilibrium** results, and the process comes to a standstill. On a large scale this difficulty is avoided by heating the calcium carbonate in such a way that the draft removes the carbon dioxide as soon as it is formed.

Lime is made by heating broken limestone or refuse marble in a narrow cylindrical furnace 50 ft. high, built of steel lined with firebrick. The best fuel is producer gas, which enters the lower part of the furnace. The shaft is kept filled with limestone, which is fed in above as the lime is removed at the bottom, so that the process is continuous. Lime is also made in the *rotary kiln* (Fig. 198), which is a cylinder 100 ft. or more in length and 8 ft. in diameter, made of steel plates and lined with fire brick. It is nearly, but not quite, horizontal, and the limestone, broken into small fragments, is fed automatically into

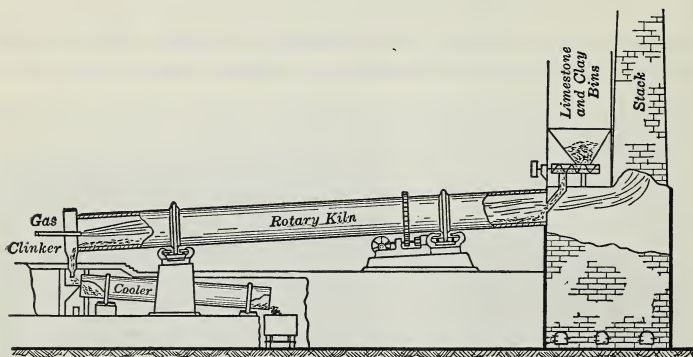


Fig. 198. Rotary kiln for lime and cement burning.

the higher end. The cylinder rotates at the rate of one complete turn in 2 minutes, and this causes the charge to travel downward through it, losing carbon dioxide and passing into lime as it goes. As the charge passes through the large flame of producer gas which enters the lower end of the kiln, the last traces of carbon dioxide are expelled, and the lime falls into the *rotary cooler*, which is seen below. The air which supports the combustion of the gas passes upward through the cooler and is pre-heated. Thus the cooler not only cools the lime, but utilizes its heat.

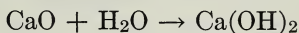
The rotary kiln is very economical both of fuel and of labor

and is widely used in "burning" lime, cement, and similar materials.

382. Properties. Lime is often gray, but the pure substance is a white, amorphous solid, 3 times as dense as water. When heated in the oxy-hydrogen flame, lime does not melt but glows brightly, forming the **lime light**. This was formerly employed for projection lanterns and in theatres, but now the electric light has almost displaced it.

Lime is a highly **refractory**¹ substance, yet it can be melted and even boiled at the temperature of the electric arc.

When a piece of lime is sprinkled with one-third of its weight of water, heat is evolved, clouds of steam escape, and the lime falls to a white powder of *calcium hydroxide*, Ca(OH)_2 , which is much bulkier than the lime from which it was made:



This same chemical change occurs slowly when lime is exposed to the air, the water vapor of the air being absorbed by the lime. Simultaneously another portion of the lime takes up carbon dioxide from the air and passes into calcium carbonate. The term **air-slaked lime** is applied to the white mixture of calcium hydroxide and calcium carbonate formed in this way.

On a large scale lime is kept in steel containers which are nearly airtight. To store it in wooden bins not only leads to spoilage, but is dangerous, since if water finds access to the lime, it may easily become hot enough to ignite the wood.

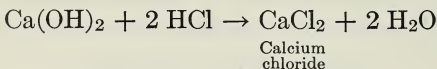
Lime is used in making mortar, in removing the hair from hides before tanning, in softening and purifying water, in the manufacture of sodium carbonate, sodium hydroxide, ammonia, bleaching powder, calcium carbide, and glass, in extracting sugar from the cane, and as a fertilizer for neutralizing acid soils.

¹ In industrial chemistry the term *refractory* is applied to substances that melt only at very high temperatures.

OTHER COMPOUNDS OF CALCIUM

383. Calcium hydroxide, $\text{Ca}(\text{OH})_2$. Calcium hydroxide, commonly called **slaked lime**, is made by thoroughly mixing lime with one-third of its weight of water. It is a white powder, with a specific gravity of 2, which dissolves in 700 times its weight of water. The clear saturated solution is called **lime water**; it is used in medicine and in the laboratory as a test for carbon dioxide.

Calcium hydroxide is an active *base*. It turns red litmus blue, and it rapidly dissolves in acids, forming solutions of calcium salts; for example:



Calcium hydroxide is now a commercial product of importance. It can be used instead of lime for many purposes, and it keeps better than the latter. It also has the important advantage over calcium oxide that no fire hazard arises in connection with it, so that it can be stored in wood and shipped in paper bags.

Slaked lime suspended in water is called **milk of lime**. **Whitewash** is simply milk of lime. After being painted on a wall, it absorbs carbon dioxide and forms a coating of calcium carbonate.

Calcimine is made by mixing slaked lime and precipitated chalk with a dilute solution of *glue*. The chalk gives smoothness to the coating, and the glue causes it to adhere more firmly than does whitewash.

Mortar is a mixture of slaked lime and sand, the sand being added to keep the mortar porous and to prevent shrinkage. The calcium hydroxide slowly absorbs carbon dioxide from the air, and the calcium carbonate formed binds the grains of sand into a stony mass.

384. Bleaching powder, CaOCl_2 . In the manufacture of *bleaching powder* a layer of slaked lime 10 cm. (4 in.) thick is spread on the floor of a long, low chamber built of concrete (Fig. 199). Chlorine is passed in and is rapidly absorbed:

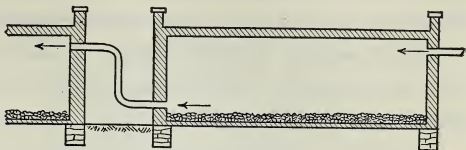
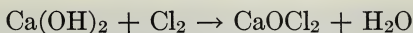
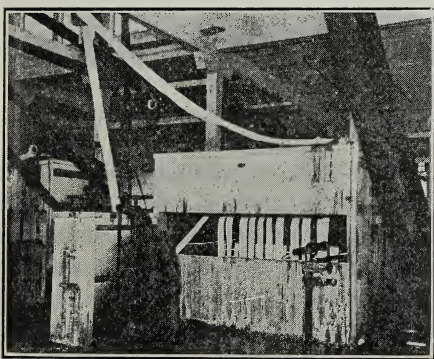
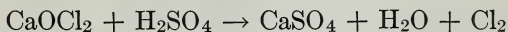


Fig. 199. Manufacture of bleaching powder.



The chamber is allowed to stand 24 hours and then ventilated, after which the finished bleaching powder is shovelled out and packed in airtight containers. The metal containers sometimes explode on being opened for the first time, and it is well to protect the eyes with goggles during the operation.

The product is a white powder which smells of chlorine. It deteriorates on preservation, more rapidly under the influence of light and warmth. With acids bleaching powder liberates chlorine:



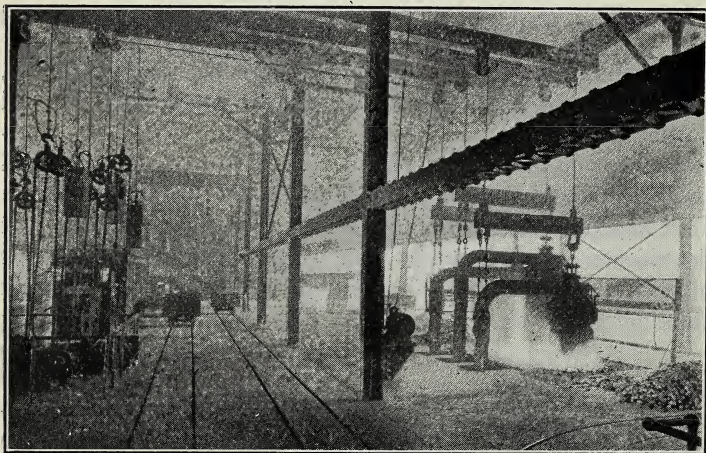
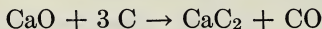
Courtesy of the H. W. Butterworth & Sons Co.

Fig. 200. Bleaching cotton yarn.

All the uses of bleaching powder depend on the fact that it yields one-third of its weight of chlorine when treated with an acid. It is a good disinfectant, but its chief application is for the bleaching of cotton and linen fabrics. The goods, sewed end to end into strips which are sometimes

50 km. (31 miles) long, are run by rolls into a dilute solution of bleaching powder and then into dilute sulphuric or hydrochloric acid, so that chlorine is set free in the fibre. Complex cleansing operations precede and follow the actual bleaching.

385. Calcium carbide, CaC_2 . Calcium carbide is made by heating a mixture of lime and coke to $1,600^\circ$ by a powerful alternating electric current:



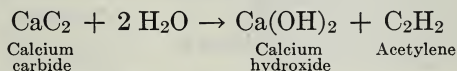
Courtesy of the American Cyanamid Co.

Fig. 201. Electric furnace for the manufacture of calcium carbide.

The furnace is a rectangular box 22 ft. by 12 ft. and 6 ft. deep, built of steel plates and lined with firebrick. The bottom is covered with a layer of blocks of graphite, which is connected with one pole of the dynamo, and over this is placed a shallow layer of crushed coke. The furnace is then filled with the charge, which consists of a mixture of 10 parts by weight of lime and 6 parts of coke, both crushed to nut size. Heavy graphite electrodes projecting from above into the mass carry a current

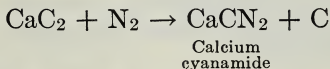
of 130 volts and 20,000 amperes, which passes through the charge to the graphite slabs in the bottom. The furnace is tapped every 45 minutes, the melted calcium carbide being allowed to run into steel cars brought up on rails, while the mixture of lime and coke is shovelled in above to keep the furnace filled. The carbon monoxide burns at the top to carbon dioxide, which escapes. Such a furnace operates day and night and produces in 24 hours 50 tons of calcium carbide.

Pure calcium carbide is colorless, but the commercial product is a hard, black mass, which is powdered for convenience in use and is shipped in steel containers closed as tightly as possible, for the carbide interacts with the moisture of the air. It is employed to generate with water the combustible gas **acetylene**, C_2H_2 , which is much used in rural districts as an illuminant:



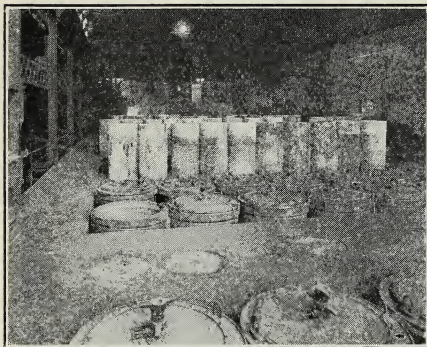
Another important use of calcium carbide is for the manufacture of *calcium cyanamide*.

386. Calcium cyanamide, $CaCN_2$. Calcium cyanamide, $CaCN_2$, which in trade is called simply **cyanamide**, is made by heating calcium carbide to $1,100^\circ$ in an atmosphere of nitrogen:



The furnace is a steel cylinder with a thick lining of firebrick, the inside dimensions being 5 ft. high by 3 ft. diameter. Such a furnace holds 1,600 lb. of pulverized calcium carbide. The nitrogen, which is obtained from liquid air (§ 228), is brought in under a slight pressure by two pipes which enter near the bottom. The heat is supplied by a long, thin carbon electrode which pierces the center of the charge and which takes at first a current of 100 volts and 200 amperes. In 20 minutes the cur-

rent is reduced to half this intensity, and after 12 hours more it is shut off, as the chemical change furnishes enough heat. After 40 hours from the beginning, during all of which time the furnace is closed as tightly as possible and the nitrogen supply



Courtesy of the American Cyanamid Co.

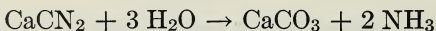
Fig. 202. Furnaces for the manufacture of calcium cyanamide.

continued, the solid cake of cyanamide is removed to be cooled and powdered for use.

Pure calcium cyanamide is white, but the commercial product, which contains only 60 per cent of real CaCN_2 , is colored black by carbon. It is much employed as a fertilizer to furnish nitrogen to plants. It should be placed upon the ground

before the crop is sown, as time is required for the transformation of the nitrogen of the cyanamide into nitrates in the soil, and until this change has occurred the cyanamide has an injurious effect on vegetation.

Another use of cyanamide is for the manufacture of *ammonia*, which can be obtained by heating cyanamide under pressure with steam in large, strong boilers (Fig. 120):



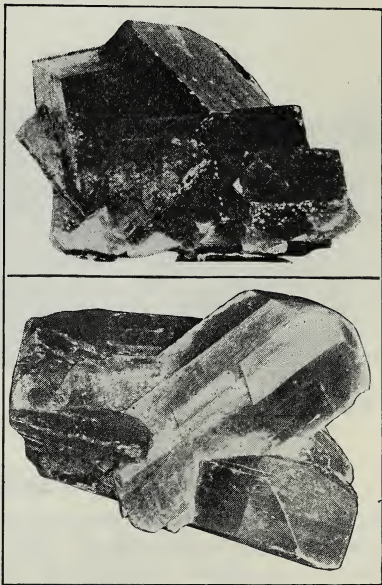
The ammonia is led off as a gas through a valve provided for the purpose.

387. Calcium chloride, CaCl_2 . Calcium chloride is a white, deliquescent solid, which is obtained in large quantities as a by-product of the manufacture of sodium carbonate by the Solvay process. Like all deliquescent substances, it is very

soluble in water. The solution freezes at a low temperature and is used instead of brine in cold-storage plants and in making artificial ice. Calcium chloride has also been employed to prevent the freezing of the water in the radiators of automobiles. When placed upon roads, calcium chloride keeps them moist and free from dust, but after a heavy rain the treatment must be repeated.

388. Calcium fluoride, CaF_2 . Calcium fluoride is the mineral **fluorite** or **fluor spar**. It is found in cubes, which may have any color but are most frequently violet. Fluor spar is mined in Illinois and is used in the preparation of *hydrofluoric acid*, HF , and as a **flux**¹ in working metals. When added to melted glass, fluor spar dissolves; on cooling it separates again in countless microscopic crystals which make the glass *translucent*. Such "opal glass" is used in shades for Welsbach and electric lights.

389. Calcium sulphate, CaSO_4 . Gypsum, which has the composition indicated by the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is the most abundant calcium mineral with the exception of cal-

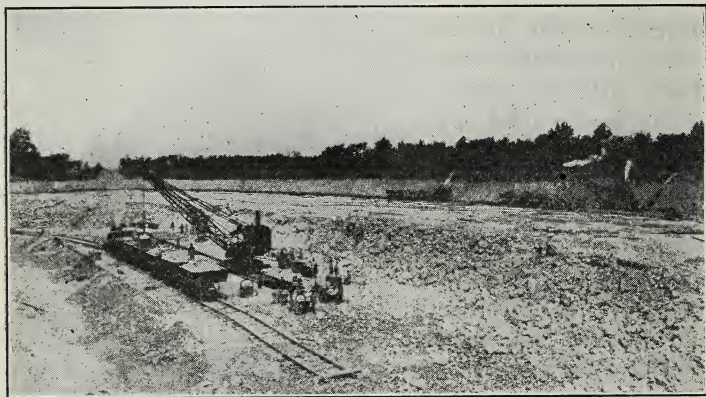


Courtesy of the American Museum of Natural History.

Fig. 203. Crystals of fluorite (above) and gypsum (below).

¹ A *flux* is a substance used in working metals. The flux melts easily, and the liquid covers the heated metal and protects it against oxidation.

cite. It occurs in flat transparent crystals or, more commonly, in glistening white masses with only a confused crystalline structure. The fact that it is soft enough to be scratched with the finger nail at once distinguishes it from other minerals of similar appearance. Gypsum is mined in Michigan, Oklahoma, and New York. It is used as a filler for paper, as a pigment, as a fertilizer on soils deficient in calcium or sulphates, and especially in making *plaster of Paris*.



Courtesy of the U. S. Geological Survey.

Fig. 204. Stripping and mining gypsum with steam shovels in a Michigan quarry.

390. Plaster of Paris, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. When gypsum is carefully heated to a temperature not exceeding 170° , three-fourths of the water escapes, and the mineral falls to a powder which contains 1 molecule of water for every 2 molecules of calcium sulphate and which is known as **plaster of Paris**. When the plaster is mixed with water, chemical combination occurs, and a stony mass of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ results, which takes the shape of any mould in which the plaster is contained.

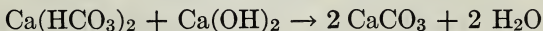
In making plaster the gypsum is crushed to 2-in. lumps and heated in an iron cylinder 10 ft. wide and 8 ft. high, which holds

12 tons and produces 10 tons of plaster. The mass is constantly stirred by a vertical shaft set with paddles which rotates about 20 times in a minute. The temperature must be carefully regulated, for if the mass is overheated, *all* of the water will escape, and the product, which in that case has the composition CaSO_4 , will not combine again with water when moistened.

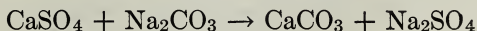
Plaster of Paris is used for surfacing inside walls. In surgery it is employed for maintaining broken limbs in a rigid position until they knit. Its use for inexpensive reproductions of statuary is familiar. Such casts are often dipped into melted paraffin, which gives them a glossy surface and makes them impervious to water.

391. Hard water. "Hardness" in water is usually due to dissolved calcium compounds. Hard water does not lather freely with soap but produces instead a sticky film which consists of a *calcium soap*. There are two kinds of hardness met with in natural waters:

Temporary hardness is due to calcium hydrogen carbonate, $\text{Ca}(\text{HCO}_3)_2$, and is removed by *boiling*, when carbon dioxide escapes and calcium carbonate deposits. Boiling, however, is expensive, and on a large scale temporary hardness is removed by adding a measured volume of *lime water*, whereby calcium carbonate is precipitated:

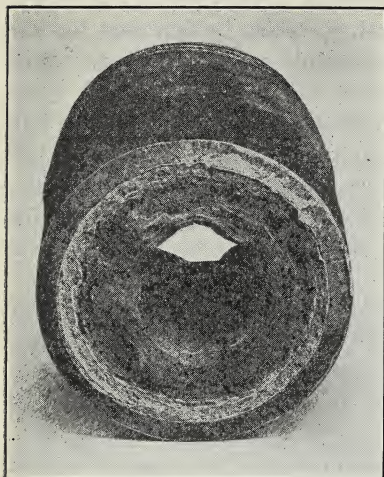


Permanent hardness is due to calcium sulphate and is unaffected by boiling. It is removed by adding a measured quantity of *sodium-carbonate* solution, whereupon calcium carbonate deposits, and sodium sulphate, which is not objectionable, remains dissolved:



In most waters both kinds of hardness are present. To

“soften” them, sodium-carbonate solution is added first and then lime water. The calcium carbonate is then allowed to settle, and the clear water drawn off for use.



Courtesy of Wm. B. Scaife & Sons Co.

Fig. 205. A badly scaled boiler tube.

One of the most serious consequences of hard water is the formation of **boiler scale**, a stony deposit of calcium sulphate in the water tubes, which results in injury to the boiler and great waste of fuel. To prevent scale it is far better to soften the water, by the method just described, before it enters the boiler than to use scale “removers” and “preventers,” many of which are put on the market and sold at extravagant prices but have little effect.

STRONTIUM (Sr=87.5); BARIUM (Ba=137)

392. Strontium and barium resemble calcium. Like it they oxidize readily in the air and rapidly liberate hydrogen from water. Compounds of strontium color the flame of the Bunsen burner *crimson*, and compounds of barium give a *green* color to the flame. These colorations are employed as *tests* for the corresponding metals.

Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, is used in fireworks, especially in making *red fire*. This is a mixture of powdered strontium nitrate with combustibles like charcoal, sulphur, or powdered shellac. **Barium nitrate**, $\text{Ba}(\text{NO}_3)_2$, is applied in the same way in making *green fire*. **Barium carbonate**, BaCO_3 , is an excellent

rat poison. **Barium chloride**, BaCl_2 , is important on account of the use of its solution as a test for sulphuric acid and sulphates, with which it forms a white precipitate of barium sulphate.

Barium sulphate, BaSO_4 , is the most abundant barium compound in nature. It occurs as the mineral **barite** in flat, tabular crystals, which are sometimes very large, and also in a white massive form which resembles marble but is much denser. The powdered substance, known in trade as **barytes**, is largely used as a filler for paper and rubber and as a pigment. Small quantities (5 per cent) add to the durability of paint, but in higher percentages it is to be regarded as an adulterant.

Barium peroxide, BaO_2 , is a white powder obtained by heating barium nitrate to redness. The residue is reheated to 600° for some time in a current of purified air. Barium peroxide is used in making hydrogen peroxide (§ 94).

SUMMARY

The members of the **Calcium Family** resemble the sodium metals, except that the calcium metals are **bivalent**.

Calcium carbonate, CaCO_3 , is the most abundant calcium compound.

Calcium is obtained by the electrolysis of melted calcium chloride.

The diet should contain abundant calcium, and the best method of making sure that the supply is sufficient is to use milk freely.

Limestone caverns, **stalactites**, and **stalagmites** owe their formation to the solubility of calcium carbonate in water containing carbon dioxide.

Calcium oxide, CaO , usually called **lime**, is made by heating calcium carbonate to a white heat.

Calcium hydroxide, $\text{Ca}(\text{OH})_2$, commonly called **slaked lime**, is an active *base*. Its clear solution is **lime water**. **Mortar** is a mixture of slaked lime and sand.

Bleaching powder, CaOCl_2 , is made by allowing slaked lime to absorb chlorine. The chlorine is liberated when the bleaching powder is treated with an acid.

Calcium carbide, CaC_2 , is obtained by heating a mixture of lime and coke in an electric furnace.

Calcium cyanamide, CaCN_2 , is formed when calcium carbide is heated in nitrogen.

Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, when gently heated loses three-fourths of its water and is converted into *plaster of Paris*, $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$.

Hardness in water is due principally to dissolved compounds of calcium. Hard water can be softened by adding calculated quantities of sodium-carbonate solution and lime water.

EXERCISES

1. Make a tabular comparison of the metals of the Calcium Family with the sodium metals. Include occurrence, properties, conduct toward air and water, flame color, valence, formulas of nitrates, chlorides, and sulphates, etc.

2. How much calcium should the diet contain per day? Why? Mention four food products rich in calcium.

3. What is the difference between marble and limestone? Why is powdered limestone or lime added to acid soils?

4. Give in detail the chemical explanation of the formation of limestone caverns, stalactites, and stalagmites.

5. Describe the production of lime in the rotary kiln.

6. What is a *refractory* substance? Give two examples.

7. Explain, with equations, the chemical composition of *air-slaked lime*.

8. Explain, with equation, the function of the bath of dilute acid in bleaching with bleaching powder.

9. Explain, with equations, the manufacture of cyanamide and the production of ammonia from the latter.

10. Distinguish, by means of formulas, between gypsum and plaster of Paris, and explain the manufacture of the latter.

11. Discuss the causes and disadvantages of hardness in water and the means of removing it.

12. Calculate the percentage composition of calcium carbonate.

13. Calculate the loss in weight when 15 grams of pure marble are heated to whiteness until the chemical change is complete.

14. 100,000 kg. of pure marble are charged into a rotary kiln. How many kilograms of lime are obtained? How many cubic meters of carbon dioxide, measured under standard conditions, escape?

15. How many tons of pure limestone must be heated to make 200 tons of lime?

16. (a) Calculate the percentage composition of barium sulphate.

(b) The mineral *witherite* is barium carbonate, BaCO_3 . Calculate its percentage composition.

17. Could air-slaked lime be employed to correct acidity of the soil? Could it be used to make mortar? Why?

18. Massive gypsum is not unlike marble in appearance. How could you distinguish the one from the other?

19. Of what two substances is old mortar chiefly composed? How could you prove your statement?

20. Why does plaster of Paris harden more rapidly than mortar?

21. How could you reconvert slaked lime into lime?

22. In hard-water districts a whitish, stony crust constantly forms in tea kettles. What is its composition?

23. Compare the properties of calcium hydroxide with those of sodium hydroxide.

REVIEW QUESTIONS

1. What is the *flame test*? Does it apply to metals or to non-metals? Name five elements that can be detected in this way, with the corresponding colors.

2. What is meant by chemical equilibrium?

3. What would happen if limestone were intensely heated in a vessel strong enough to withstand the pressure produced? Why is a limekiln always so constructed that the draught from the fire on its way to the chimney sweeps through the charge of limestone?

CHAPTER XXXII

GROUP IIB. THE ZINC FAMILY

MAGNESIUM, ZINC, CADMIUM, MERCURY

393. General. The metals of the Zinc Family are white metals, which retain their lustre in dry air and are affected very slowly, if at all, by water. They form oxides when heated in the air. Magnesium, zinc, and cadmium occur only in compounds. Mercury is found both native and in compounds. The metals of the zinc family are *bivalent*. Mercury is bivalent in the *mercuric* compounds, but it is *univalent* in the *mercurous* compounds.

MAGNESIUM (Mg=24.3)

394. Occurrence. Magnesium is so common in its compounds that it ranks sixth among the elements in abundance and constitutes 2.27 per cent of the crust of the earth. **Magnesite**, which is magnesium carbonate, MgCO_3 , is a white mineral which is largely used in the manufacture of heat-insulating coverings for boilers and steam pipes and of refractory brick for very high temperatures. **Dolomite** is a double carbonate of calcium and magnesium, $\text{CaCO}_3 \cdot \text{MgCO}_3$. It is abundant, making up whole mountain ranges in some localities, and it is used as a raw material for the manufacture of refractories and of magnesium compounds. **Talc**, **soapstone**, and **meerschaum** are silicates¹ of magnesium. **Asbestos** is a silicate of calcium and magnesium. **Carnallite**, which occurs at Stassfurt, Germany, and in Alsace, is a chloride of potassium and magnesium, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. It is used as a potassium fertilizer and in

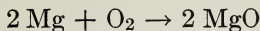
¹ A *silicate* is a compound of a metal with silicon and oxygen.

the preparation of magnesium. The very important mineral **kainite** has the composition expressed by the formula $\text{KCl} \cdot \text{MgSO}_4 \cdot 3 \text{H}_2\text{O}$. It is found in the same localities and is widely used as a fertilizer. Magnesium compounds frequently occur dissolved in natural waters. In large quantity they produce *hardness* similar to that caused by calcium compounds and removable by the same methods.

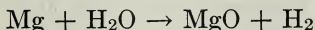
395. Preparation. When carnallite is gently heated, the water of crystallization escapes, and the residue has the composition expressed by the formula $\text{KCl} \cdot \text{MgCl}_2$. This is melted in an iron crucible and electrolyzed. The crucible forms the cathode, the anode being a stick of graphite which projects into the liquid. Magnesium collects under the melted carnallite, which covers and protects it from oxidation.

396. Properties. Magnesium is a brilliant white metal, which becomes dull in moist air but is not seriously attacked. Its specific gravity is 1.75, so that it is lighter than glass and far less dense than the familiar metals. It melts easily and can be purified by distillation, for it boils at a bright red heat.

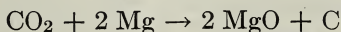
Heated in air, magnesium ignites and burns with a brilliant flame, producing a dense smoke and a white residue, both of which consist of magnesium oxide, MgO :



In pure oxygen the combustion is dazzling, and the glass vessel in which it is carried out is usually broken. When burning magnesium is plunged into *steam*, the combustion continues with undiminished intensity, hydrogen being liberated:

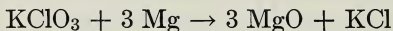


Burning magnesium also continues its combustion in carbon dioxide, with separation of carbon in the form of lamp black:



When heated in nitrogen, magnesium absorbs the gas, forming a yellow powder of *magnesium nitride*, Mg_3N_2 . This explains its use by Ramsay in separating argon from air (§ 220).

397. Uses. The dazzling light of burning magnesium is rich in the wavelengths that affect photographic films and plates. *Flashlight powders* consist of a mixture of powdered magnesium with some substance rich in oxygen, the presence of which increases the energy of the combustion. Potassium chlorate is often used for this purpose:

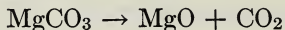


Magnesium is also used in fireworks. It was largely used during the World War in the manufacture of star shells, flares, and rockets for lighting up battlefields at night.

Aluminum melted with small percentages of magnesium yields a white alloy called **magnalium**, which is light and strong, retains its lustre in the air, and works well on a lathe. The percentage of magnesium depends somewhat upon the use that is to be made of the alloy but averages about 6 per cent. Magnalium is used for the scales of optical instruments and for the beams of balances. For many applications in which strength, lightness, and rigidity are important, it is displacing aluminum.

COMPOUNDS OF MAGNESIUM

398. Magnesium oxide, MgO . Magnesium oxide, commonly called **magnesia**, is the product of the burning of magnesium, but it is made commercially by the much cheaper method of heating *magnesium carbonate*, MgCO_3 , which decomposes like calcium carbonate but at a lower temperature:



Magnesium oxide is a pure white powder, which seems extremely light on account of its porosity, though the actual

density of the grains is over 3. It is almost insoluble in water, melts only in the electric arc, and, because of the large amount of air retained by it, it is a remarkably bad conductor of heat. Thus it forms the best of all refractories for very high temperatures and of heat insulators for covering pipes conveying hot water or steam. One end of a brick made of magnesium oxide may be at a bright white heat while the other is scarcely warm to the touch. Impure grades of magnesium oxide, suitable for furnace brick, are made by calcining magnesite or highly magnesian limestone.

Pure magnesium oxide is prepared by calcining artificial magnesium carbonate prepared for the purpose. It is used as a polishing and cleansing powder, and in medicine as a laxative and as an antidote when acids have been swallowed.

399. Magnesium carbonate, MgCO_3 . Magnesium carbonate occurs in nature as **magnesite**, the purer grades of which are imported from Greece. Magnesite pure enough to serve as an excellent material for making firebrick occurs in California and in Austria.

Magnesium carbonate is prepared artificially by adding a solution of sodium carbonate to a boiling solution of magnesium sulphate, washing the white precipitate, and drying. The product, which is known in pharmacy as "**magnesia alba**," consists partly of magnesium carbonate and partly of magnesium hydroxide, $\text{Mg}(\text{OH})_2$. Both pass into magnesium oxide when the **magnesia alba** is heated. The magnesium oxide prepared in this way is used in medicine under the name "**calcined magnesia**."

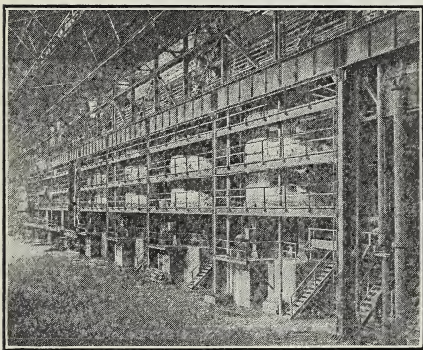
400. Magnesium sulphate, MgSO_4 . Magnesium sulphate forms colorless crystals which have the composition $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$. It has long been employed in medicine under the name "**Epsom salt**."

Magnesium citrate is the magnesium salt of citric acid, $\text{C}_6\text{H}_8\text{O}_7$. It is largely used in medicine under the name "***citrate of magnesia***."

ZINC ($\text{Zn} = 65.5$)

401. Occurrence. The most important ore of zinc is the *sulphide*, ZnS , which is called **zinc blende** or "black jack" by the miner and **sphalerite** by the mineralogist, and which occurs abundantly in Missouri, Wisconsin, Iowa, and Illinois. *Zinc carbonate*, ZnCO_3 , is the mineral **smithsonite**, often called by the miners' name of "drybone." **Franklinite** is a black, impure zinc oxide containing iron and manganese which occurs at Franklin Furnace, New Jersey, and is in that one locality an important ore of zinc.

402. Extraction. Most of the zinc of commerce is obtained from zinc sulphide. The ore is heated in a current of air until

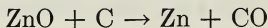


Courtesy of the Anaconda Copper Co.

Fig. 206. Battery of mechanically stirred furnaces for roasting zinc sulphide ore.

the sulphur is removed as sulphur dioxide, the zinc at the same time passing into zinc oxide. The zinc oxide is mixed with coke and placed in a retort, roughly semicircular in cross-section, about 6 ft. long by $1\frac{1}{2}$ ft. high (Fig. 207). A number of such retorts (m, m) are placed in the same furnace and heated by

a flame of producer gas. The chemical change is represented by the equation:



The zinc, owing to the high temperature, is liberated as a vapor, most of which condenses in the fire-clay receiver v . In the sheet-iron tube a some of the zinc that escapes condensation in

v collects as a gray powder called *zinc dust*, which goes back into the retort with the next charge.

The zinc obtained by this method is called in trade "**spelter**," and is pure enough for industrial uses. For scientific purposes zinc can be purified by distillation. The chief impurities in spelter are carbon, iron, arsenic, and cadmium (§ 410). The United States is the chief producer of zinc among the nations.

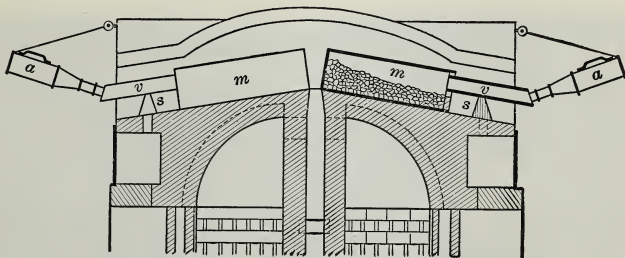
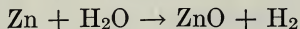


Fig. 207. Retorts for the reduction of zinc oxide.

403. Physical properties. Zinc is a bluish-white metal with a specific gravity of 7.1, which melts at 419° and boils at 930° . Zinc as prepared from the ore is hard and brittle, but when heated somewhat above the boiling point of water, it becomes soft and can be rolled into sheets which then retain their malleability when cold. This behavior of zinc is of great importance in the utilization of the metal.

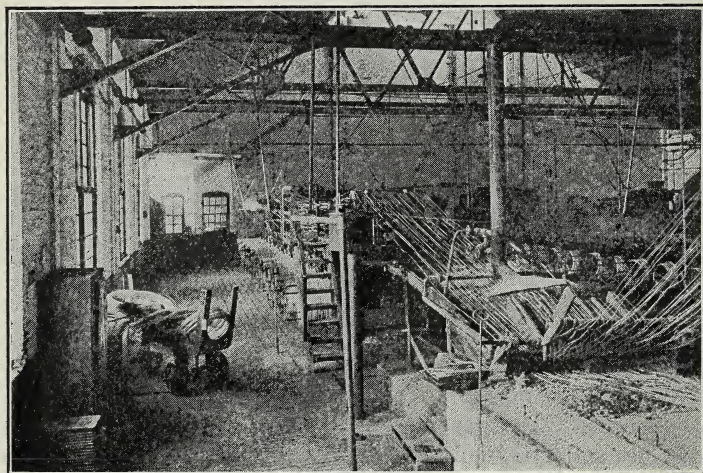
404. Chemical conduct. Heated in air or oxygen, zinc burns with a bluish flame to a white smoke of zinc oxide, ZnO . It scarcely affects water, even when boiled with it, but steam led over heated zinc is rapidly decomposed, with liberation of hydrogen and formation of zinc oxide:



The white rust that forms on zinc in moist air contains both the hydroxide and the carbonate of the metal. Its formation

is slow, and for practical purposes zinc resists the action of the weather excellently, even under severe conditions.

Pure zinc is scarcely affected by acids, because the hydrogen first formed adheres to the metal in a thin, continuous film and prevents the acid from coming into further contact with it. In generating hydrogen in the laboratory it is usual to avoid this difficulty by adding a few drops of a solution of copper sulphate



Courtesy of the American Steel & Wire Co.

Fig. 208. Galvanized iron wire emerging from the zinc bath.

to the gas bottle containing zinc and water before introducing the acid. This coats the zinc with copper, from which the hydrogen produced when the acid is added escapes without difficulty.

405. Uses. About two-thirds of the total output of zinc is consumed in “galvanizing” iron and steel. The object is first freed from rust by soaking it in dilute sulphuric acid, a process which is called “pickling,” and is then dipped into melted zinc, which plates the surface of the iron. The surface

of the zinc is kept covered with a layer of ammonium chloride to prevent oxidation. The finished product contains about one-eighth of its weight of zinc and shows a very satisfactory resistance to rust.

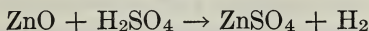
Zinc is employed in roof gutters and for making dry cells and other batteries. Considerable quantities of zinc are made into *alloys*, especially brass and German silver. The manufacture of the important pigment *zinc oxide* also consumes a large tonnage of zinc. In the school laboratory zinc is used for generating hydrogen with acids. The "mossy" zinc employed for this purpose is made by pouring melted zinc slowly into water.

COMPOUNDS OF ZINC

The compounds of zinc in many respects resemble those of magnesium, but although the compounds of magnesium have little injurious action on the body, those of zinc are *poisonous*. For this reason water intended for drinking should not be allowed to stand in vessels of galvanized iron, since, especially if the water is rich in carbon dioxide, sufficient zinc may dissolve to render it unfit for consumption.

406. Zinc oxide, ZnO. Zinc oxide occurs sparingly as the mineral *zincite*. Commercially, zinc oxide is made by heating zinc in fire-clay retorts until the metal boils. The vapor is led into a flue through which air is drawn. Here the zinc burns to zinc oxide, which is caught by passing the air through large bags of cotton cloth. Instead of zinc a mixture of roasted zinc ore and coke is often used, zinc vapor being liberated and oxidized as above.

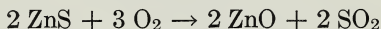
Zinc oxide is a pure-white powder, which becomes lemon-yellow when heated but returns to its white color on cooling. It is insoluble in water but dissolves in acids, forming zinc salts; for example:



Zinc oxide is largely used as a pigment under the name **zinc white**. It is especially employed for indoor work. It yields a paint which dries with a smooth, glossy surface, whereas the surface produced by a pure white-lead paint is dull. The brilliant "enamel" paints so much used at present contain as a pigment pure zinc white, mixed with linseed oil, turpentine, and varnish. For outside painting, mixtures containing white lead and zinc white are in use. This gives a more durable paint film than either alone.

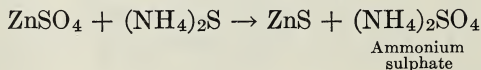
Large quantities of zinc oxide are employed as a filler for rubber, especially for automobile tires. The tread of a tire may contain half its weight of zinc oxide, which gives toughness and wearing qualities. It is also used as a filler in celluloid and in the manufacture of linoleum, oil cloth, and printing ink. The preparation known in pharmacy as **zinc ointment** is made by incorporating zinc oxide with lard or other fat.

407. Zinc sulphide, ZnS. Zinc sulphide is the mineral **sphalerite** or **zinc blende**, the most abundant ore of zinc. It occurs in crystalline masses which often resemble rosin in color and lustre (Fig. 34). When heated in a current of air, zinc sulphide gives off sulphur dioxide, and *zinc oxide* remains:



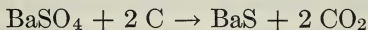
Heating the sulphide of a metal in a current of air to convert it into an oxide is known as **roasting** in metallurgy. The oxide is afterward heated with coke in order to obtain the metal.

Zinc sulphide is insoluble in water and is precipitated as a white amorphous powder when a solution containing a zinc salt is mixed with a solution of *ammonium sulphide*, $(\text{NH}_4)_2\text{S}$:

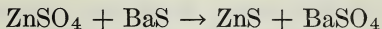


The cheap and excellent pigment **lithopone**, which is widely used as a first coat for inside work, is a mixture of zinc sulphide

and *barium sulphate*. In making it, finely powdered mineral barium sulphate is heated to redness with coke, which converts it into barium sulphide, BaS:

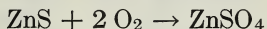


The barium sulphide is then dissolved in water and added to a solution of zinc sulphate, whereupon a white precipitate forms which consists of zinc sulphide and barium sulphate:



In order to produce a pigment of good covering power it is necessary to dry this mixture, heat it to redness, cool it suddenly in cold water, and grind it wet.

408. Zinc sulphate, ZnSO_4 . Zinc sulphate is produced when zinc dissolves in dilute sulphuric acid. On a large scale it is made by the careful roasting of mineral zinc sulphide at a low red heat:



From the roasted mineral the zinc sulphate is extracted with warm water, which on cooling deposits crystals corresponding to the formula $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, which have long been known as “white vitriol.” The resemblance of white vitriol to Epsom salt is so close that confusion between the two has led to accidents, for zinc sulphate is poisonous. It is used in dyeing and calico printing and in the preparation of lithopone. In medicine zinc sulphate finds application as a powerful astringent and, in very dilute solution, as an eye wash.

409. Zinc chloride, ZnCl_2 . When zinc or zinc oxide is dissolved in hydrochloric acid, zinc chloride is produced and can be obtained by evaporating as a colorless, crystalline, deliquescent mass, which is very soluble in water and quite poisonous. Zinc chloride is used in surgery as a caustic, and its solution is employed as an embalming fluid and to impregnate

timber, which it protects against decay. A solution of zinc chloride made by dissolving zinc in hydrochloric acid is used to cleanse the surface of metals before soldering. It removes films of rust which would otherwise weaken the joint. This solution is poisonous, and it must be employed with care in soldering tins containing food products.

An important application of zinc chloride is the production of *vulcanized fibre*, which is made by passing paper over heated rolls into a concentrated solution of zinc chloride. The surface is gelatinized, so that many sheets can afterward be rolled together into a block of any desired thickness. The zinc chloride is then washed out, and the fibre dried.

Well-made vulcanized fibre may possess three times the strength of leather. It is used for trunks, washers, valves, drawing triangles, and the like. It is an excellent insulator and finds increasing application in the electrical industry.

CADMIUM (Cd = 112)

410. Most zinc blende contains about 0.3 per cent of **cadmium**, which is darker in color and denser than zinc and has a lower melting point and boiling point. Some of the alloys of cadmium with tin, lead, and other metals melt at very low temperatures and are called *fusible metals*. The main use of cadmium is in the production of these alloys, which have a wide field of usefulness in the electrical industry and in automatic sprinkling devices for protection against fire.

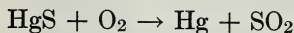
Cadmium sulphide, CdS, usually called **cadmium yellow**, is employed as a fine pigment and in coloring toilet soaps.

MERCURY (Hg = 200)

411. Occurrence. The only important ore of mercury is **cinnabar**, which is *mercuric sulphide*, HgS. Cinnabar can easily be distinguished from other minerals by its red color, by

its high specific gravity (8), and by the fact that when heated it vaporizes without leaving any residue. Cinnabar is mined in Spain and Italy. In the United States valuable deposits of the mineral exist at New Almaden, California, and in Nevada and Texas.

412. Extraction. When cinnabar is roasted, sulphur dioxide escapes, but mercuric oxide cannot be formed because it is decomposed by heat. Hence the chemical change takes the direction indicated by the equation:



The mercury is swept along as vapor in the current of furnace gases, and its condensation is the main difficulty in the process of extraction.

Figure 209 is a diagram of the blast furnace and of a portion of the condensing apparatus. The mixture of lumps of ore with charcoal is placed in the cup-shaped space at the top of the shaft *A*, and when the cone *c* is lowered, the charge slides into the furnace. Air is admitted through the perforated tube which projects into the bottom of the furnace, and exhausted ore is removed through the inclined canals at right and left of the diagram.

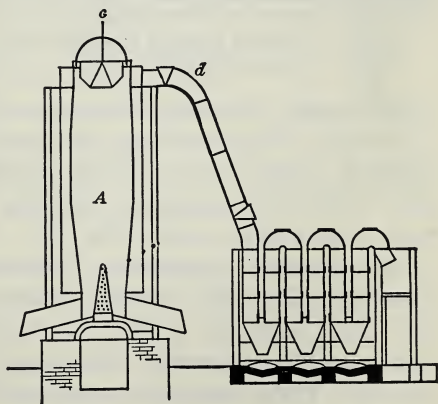
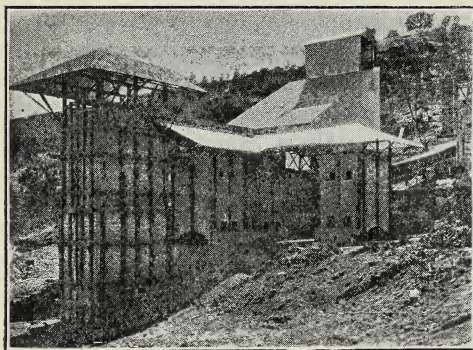


Fig. 209. Furnace for the roasting of cinnabar.

By means of *d* the gases are led through a number of U-shaped earthenware pipes. These open at the bottom into a cement trough partly filled with water, under which the mer-

cury collects. The gases then pass through long underground wooden passages and brick chambers to complete the condensation.

Mercury obtained in this way contains traces of other metals, especially zinc, tin, and bismuth. A rough test for



Courtesy of the California State Mining Bureau.

Fig. 210. Mercury smelting plant with brick condensing chambers.

purity is to place upon white paper a drop of the metal and to cause it to move about by inclining the paper. Impure mercury forms a tarnished globule which is drawn out to a tail and moves sluggishly.

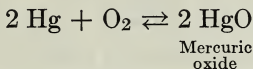
Mercury can be purified by careful distillation in iron

vessels. The impurities, not being volatile at the boiling point of mercury, remain behind. Or, the impure metal is allowed to fall in a thin stream through a long column of dilute nitric acid, which, while scarcely affecting the mercury, dissolves from it the foreign metals (Fig. 211).

413. Physical properties. Mercury is a dense, bright, metallic liquid, with a specific gravity of 13.56, which freezes at -38.9° and boils at 357° . It is a good conductor of electricity, and its expansion with rising temperature is large and regular. These properties, along with its high density, form the basis of many of the industrial and scientific applications of the metal. Mercury vaporizes slowly at ordinary temperatures, and a bit of gold leaf suspended over it in a bottle becomes whitened by mercury deposited upon the gold. The specific gravity of mercury vapor shows that the molecule of mercury

contains but one atom. Hence *the formula is identical with the symbol.*

414. Chemical conduct. When mercury is heated to boiling in the air, oxygen is slowly absorbed, and a red film of *mercuric oxide* collects on the surface of the metal:



The reaction is reversible, for if the mercuric oxide is heated to a higher temperature, it is decomposed into mercury and oxygen.

When mercury is heated in a test tube with sulphur, a dark mass of mercuric sulphide is obtained, which on being powdered becomes bright red. The same combination occurs more slowly when mercury and sulphur are rubbed together in a mortar.

In the electromotive series (§ 372) mercury comes just before silver, platinum, and gold, so that most of the common metals, when dipped into a solution of a mercury salt, become plated with mercury or with a white alloy of mercury and the metal.

Mercury is not affected by hydrochloric acid or by dilute sulphuric acid. Concentrated sulphuric acid converts it into *mercuric sulphate*, HgSO_4 . Cold dilute nitric acid converts mercury into a solution of *mercurous nitrate*, HgNO_3 , and warm concentrated nitric acid yields *mercuric nitrate*, $\text{Hg}(\text{NO}_3)_2$.

With the exception of iron, all the familiar metals unite directly with mercury, forming white, lustrous alloys which are called **amalgams**. These are crystalline solids when pure, but as usually made they contain an excess of mercury and are

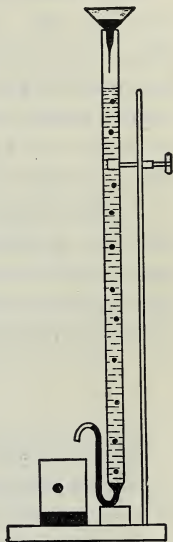


Fig. 211. Purification of mercury by nitric acid.

pasty masses or stringy liquids. *Silver amalgam* is soft when freshly prepared but rapidly becomes very hard. It is used in filling teeth. *Tin amalgam*, which behaves in a similar way, was formerly used in making mirrors.

415. Uses. Mercury is employed in the extraction of gold from its ores. On account of its high density it is used in filling barometers. A column of mercury only 30 in. high balances the pressure of the air, whereas a column of water to do the same would have to be nearly 34 ft. in height. On account of its large and regular expansion with rising temperature, mercury makes an excellent thermometric fluid.

“**Blue ointment**,” made by rubbing mercury with fat, is used in medicine. Considerable quantities of mercury are consumed in making useful compounds of the metal, particularly *mercuric oxide*, *mercuric sulphide*, *mercuric chloride*, and *mercurous chloride*.

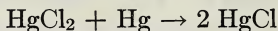
COMPOUNDS OF MERCURY

Mercury forms two series of compounds:

In the **mercurous** compounds the mercury atom is *univalent*, as in *mercurous chloride*, HgCl , and *mercurous nitrate*, HgNO_3 .

In the **mercuric** compounds the mercury atom is *bivalent*, as in *mercuric oxide*, HgO , *mercuric chloride*, HgCl_2 , and *mercuric nitrate*, $\text{Hg}(\text{NO}_3)_2$.

416. Mercurous chloride, HgCl . Mercurous chloride is the important drug **calomel**. It is made by heating a mixture of 3 parts of mercury with 4 parts of mercuric chloride:



The mercurous chloride vaporizes and condenses on the cover of the vessel as a dense white cake, which is powdered and washed with water to remove the poisonous mercuric chloride which it usually contains.

Mercurous chloride is a heavy, white, tasteless powder,

insoluble in water. On the application of heat it **sublimes**, that is, it vaporizes without melting and condenses in the cool upper part of the vessel to a solid which is called a **sublimate**. Exposure to light changes mercurous chloride to a mixture of mercuric chloride and mercury, darkening the color:



In the household, therefore, calomel tablets should be protected from light and should not be used after they have become blackened.

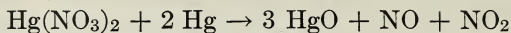
417. Mercuric chloride, HgCl_2 . Mercuric chloride, commonly called **corrosive sublimate**, is made by heating mercury in chlorine. It is a dense, white substance which crystallizes in needles. Unlike mercurous chloride, mercuric chloride *melts* when heated, and the liquid at a slightly higher temperature passes into vapor. It differs from mercurous chloride also in being soluble in water, in having a bitter, nauseous taste, and in being intensely *poisonous*.

Mercuric chloride forms an insoluble compound with the *albumin* of eggs and other food products. Hence the best antidote for it is raw eggs taken at once, or if eggs are lacking, copious draughts of milk.

Mercuric chloride is an excellent *antiseptic* and is widely used in surgery for that purpose. In the home a solution of mercuric chloride in 2,000 times its weight of water is employed to wash out slight wounds, but it should only be used when there is reason to fear that the cut is infected. *Each of the mercuric-chloride tablets of the household contains about twice the fatal dose of the poison.* They should be locked up by themselves in a safe place. The custom of keeping them in a medicine closet side by side with comparatively harmless materials has been the cause of many accidents.

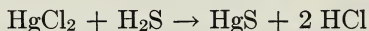
418. Mercuric oxide, HgO . In making mercuric oxide on a large scale, mercury is dissolved in nitric acid, and the solution evaporated to dryness to obtain mercuric nitrate,

$\text{Hg}(\text{NO}_3)_2$. This is then mixed with an equal weight of mercury and heated until gas no longer escapes:



Mercuric oxide is a dense, brick-red, crystalline powder, which turns black when gently heated and separates into its elements at a red heat. Under the name "**red precipitate**" it is employed in pharmacy in the preparation of ointments and for the destruction of vermin. Its largest use is as a constituent of the "**anti-fouling paint**" which is applied to ships as an outer coating below the water line. The presence of the poisonous mercuric oxide keeps the hull free from barnacles.

419. Mercuric sulphide, HgS . Mercuric sulphide can be obtained by passing hydrogen sulphide into a solution of mercuric chloride:



or by patiently rubbing in a mortar a mixture of sulphur with about 6 times its weight of mercury.

Prepared by either method, mercuric sulphide is a dense, jet-black powder. When the black powder is gently heated, it sublimes, and the sublimate when powdered is bright *red* in color. The important pigment **vermilion** consists of this red modification of mercuric sulphide. In making it a mixture of sulphur and mercury is placed in a barrel, which rotates on a horizontal axis, and is left there several hours until the combination is complete. The mercuric sulphide is then transferred to a tall earthenware cylinder and is sublimed by a gentle heat. The powdered sublimate is the vermilion of commerce.

Vermilion is a heavy, bright-red pigment, which is unaffected by light, by the weather, and by the linseed oil, turpentine, and other substances that are mixed with it in preparing paint. However, it is expensive, and its high density causes it to settle out of the oil and makes it difficult for the painter to apply an even coat.

SUMMARY

The most abundant **magnesium minerals** are *magnesite*, MgCO_3 , and *dolomite*, $\text{CaCO}_3 \cdot \text{MgCO}_3$.

Magnesium is prepared by the electrolysis of potassium magnesium chloride, $\text{KCl} \cdot \text{MgCl}_2$.

Magnesium oxide is made by heating magnesium carbonate. It is used as a refractory and in medicine.

Crystallized **magnesium sulphate**, commonly called "**Epsom salt**," corresponds to the formula $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$.

Zinc blende, *black jack*, or *sphalerite*, ZnS , is the chief **ore of zinc**. To extract the zinc the ore is roasted to zinc oxide, which is then reduced by heating to whiteness with coke.

The most important *use* of zinc is for coating iron and steel as a protection against rust.

Brass and **German silver** are useful **alloys** of zinc.

Zinc oxide is an important white pigment and filler.

The white pigment **lithopone** is a mixture of zinc sulphide and barium sulphate.

Cadmium resembles zinc and is found in zinc ores.

The only **ore of mercury** is *cinnabar*, which is **mercuric sulphide**, HgS .

Mercury is used in extracting gold from its ores, in filling thermometers and barometers, and in making important compounds, especially *calomel*, HgCl ; *corrosive sublimate*, HgCl_2 ; *red precipitate*, HgO ; and *vermilion*, HgS .

EXERCISES

1. What is the difference between *magnesium* and *magnesia*?
2. What is a *refractory*? Why is *magnesia* useful as a refractory?
3. How is *zinc white* made? What are its main uses?
4. Why does galvanized iron resist so well the action of the weather?
5. Make a tabular comparison of *calomel* and *corrosive sublimate*. Devise a method of distinguishing the one from the other.

6. How is the pigment *vermilion* obtained?

7. The electric current is passed through fused $\text{KCl} \cdot \text{MgCl}_2$ until 14 grams of magnesium are produced. How many liters of chlorine, measured under standard conditions, are liberated? ($\text{KCl} \cdot \text{MgCl}_2 \rightarrow \text{KCl} + \text{Mg} + \text{Cl}_2$.)

8. How many liters of oxygen are needed to burn 9 grams of magnesium?

9. Mercurous chloride contains 84.93 per cent of mercury and 15.07 per cent of chlorine. What is the atomic weight of mercury if that of chlorine is 35.5?

10. Mercuric chloride contains 73.8 per cent of mercury and 26.2 per cent of chlorine. What is the atomic weight of mercury if that of chlorine is 35.5?

11. A solution of zinc chloride is *acid* to litmus. What does this indicate?

12. What would be the composition of lime prepared by calcining dolomite?

13. Devise two methods of obtaining carbon dioxide from magnesite.

14. Why are paints made of zinc oxide not discolored by hydrogen sulphide?

15. How could you distinguish mercuric nitrate from silver nitrate?

16. Name two important alloys of zinc. What is an *amalgam*?

REVIEW QUESTIONS

1. Name the metals discussed thus far that are obtained by electrolysis. Are they light or heavy metals?

2. What use was made of magnesium in preparing argon from air?

3. Where do the elements of the Zinc Family stand in the electrochemical series? Which one is found in the free state in nature? Why?

4. Using the electrochemical series, devise an easy method of testing a water solution for mercury.

5. State the law of multiple proportions. Illustrate it by the two chlorides of mercury.

CHAPTER XXXIII

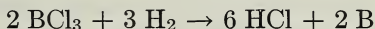
GROUP III. BORON AND ALUMINUM

Both the elements of this group are always *trivalent*.

BORON (B=11)

420. Occurrence. *Boron* has not been found native. *Boric acid*, H_3BO_3 , occurs in Italy and serves in Europe as the chief source of the boron compounds of commerce. Deposits of **borax**, which is a *borate of sodium*, exist in California, but in the United States compounds of boron are prepared mainly from the mineral **colemanite**, which is *calcium borate* and which is found abundantly in California and Nevada.

421. Preparation. Pure boron is obtained by heating a mixture of hydrogen with the vapor of *boron chloride*, BCl_3 , by means of an electric arc:



Boron is a gray, amorphous solid, insoluble in water and about as hard as the diamond. Its electrical resistance *decreases* rapidly with increasing temperature, and this unusual property will doubtless lead to important applications in the electrical industry.

422. Boric acid, H_3BO_3 . In northern Italy, 20 miles north-east of the city of Florence, is a volcanic region in which jets of steam containing the vapor of **boric acid** issue from the rocks. When the steam is made to bubble through water, the latter becomes charged with boric acid. The solution thus obtained is evaporated in shallow lead pans, beneath which volcanic steam is passed, until the liquid is sufficiently concentrated to deposit boric acid on cooling.

In the United States, boric acid is made by treating *colemanite* with sulphuric acid, which yields calcium sulphate and boric acid.

Boric acid was formerly called **boracic acid**. It forms colorless scales which have a greasy feel and dissolve in 25 times their weight of cold water. The solution scarcely reddens blue litmus and is a very poor conductor of the electric current, for boric acid is one of the feeblest of acids and is very slightly ionized.

Boric acid is an antiseptic, and it has been employed to prevent the decay of food products. It has often been detected in ice-cream cones. It is a frequent constituent of toilet powders for relieving inflamed conditions of the skin. Its solution in 50 times its weight of distilled water is largely employed as an eye wash.

423. Borax, NaB_4O_7 . Borax is made in Europe by treating boric acid with a solution of sodium carbonate:



In the United States borax is obtained by boiling *colemanite* with sodium-carbonate solution, which results in the formation of calcium carbonate and borax.

Borax forms colorless crystals which correspond to the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and are freely soluble in water, forming a solution which is strongly alkaline to litmus and other indicators. When heated, the crystals swell up, give off steam, and melt to a transparent mass of $\text{Na}_2\text{B}_4\text{O}_7$, which is often called **borax glass**.

Borax is employed in the household for cleansing and for softening hard water. It is a frequent constituent of soaps. It is used as a flux in soldering and brazing and finds application also in the manufacture of glass. The largest use of borax is in the preparation of the enamel glazes for "agate" cooking utensils.

424. Test for boric acid and borates. Boric acid is soluble in alcohol, and the solution burns with a *green flame*. This behavior is applied as a *test* for boric acid. In testing borates, like colemanite or borax, the powdered substance is first mixed with a little sulphuric acid, to liberate boric acid. A little alcohol is then added, and the mixture ignited.

ALUMINUM (Al=27)

425. Occurrence. Although aluminum does not occur native, its compounds are so widespread that it follows oxygen and silicon in point of abundance, coming third in order of the elements and making up 7.84 per cent of the crust of the earth. From one-tenth to one-fifth of the weight of the soil is composed of aluminum compounds, and the only important rocks that do not contain them are limestone and sandstone.

The vast quantity of aluminum in the rocks is present as *silicates*, which contain, in addition to the aluminum, other metals, especially potassium, magnesium, sodium, iron, or calcium. Among these rock-forming silicates of aluminum are *feldspar*, *mica*, and *garnet*.

Feldspar, which is a *silicate of aluminum and potassium*, is one of the most abundant of minerals. Under the action of the weather the potassium is slowly removed, and the feldspar crumbles to a mass of **clay**, which is *aluminum silicate*. Clay is white when pure, but it is usually colored yellow, red, or blue by impurities. This disintegration of feldspar is a most important chemical change, for it is the cause of the formation of *soil*.

Among the useful aluminum minerals are *corundum*, Al_2O_3 , *bauxite*, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and *cryolite*, Na_3AlF_6 . Bauxite is the principal source of the metal.

426. Extraction. The manufacture of aluminum rests upon the fact that aluminum oxide, when dissolved in a suitable liquid, is decomposed by the electric current, the aluminum separating at the negative pole, the oxygen at the positive.

The solvent that has been found best for the purpose is the melted mineral *cryolite*. The cryolite is contained in the rectangular iron box shown in Figure 212, which is 8 ft. long, 4 ft. wide, and 2 ft. deep. The box is lined with carbon and is connected with the negative pole of a dynamo. The carbon rods shown in the diagram form the positive pole. The metal support of these rods is connected with the box by a *shunt*¹ in

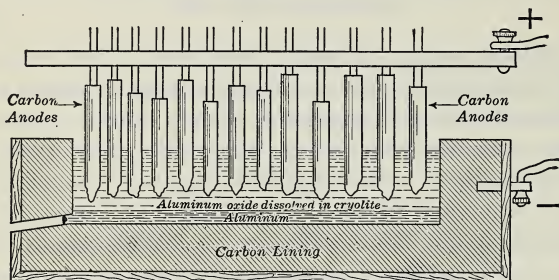


Fig. 212. Diagram of the electrolytic extraction of aluminum.

which there is an incandescent lamp, so that the electric current can pass either through the lamp or through the liquid in the box.

The aluminum oxide used must be pure, for once the aluminum is made, it cannot be refined. The aluminum oxide is prepared from **bauxite** by a long and careful process of purification. It is dried by being allowed to rest upon the surface of the melted cryolite in the box, a proceeding which also serves the purpose of protecting the eyes of the workmen from the glare.

When there is plenty of aluminum oxide dissolved in the bath, the current passes mainly through the liquid, because it offers less resistance than does the lamp, but when the dis-

¹ A shunt is a second path provided for the electric current, so that the current can follow either path according to the respective resistances.

solved aluminum oxide is nearly all decomposed, the resistance of the bath becomes high, and enough current passes through the lamp to cause it to light up. Then the workman in charge stirs aluminum oxide into the bath until the lamp is darkened.

The aluminum collects as a liquid beneath the melted cryolite and is tapped off from time to time. The oxygen combines with the carbon of the anodes and escapes as carbon dioxide. The cryolite remains unaltered.

The process just described is the work of an American chemist, Charles Martin Hall, who devised it while a student at Oberlin College. It was independently invented shortly after by a French metallurgist, Héroult. It has transformed aluminum from a scientific curiosity into one of the most familiar and useful of the metals.

427. Physical properties.

Aluminum is a gray metal which will take a high polish. In hardness and strength it compares favorably with many metals, but it is inferior to steel in these respects and will never serve as a substitute for the latter. It is ductile and malleable both hot and cold, and it is a good conductor of electricity and heat.

Aluminum melts at 660° . Its most striking property is its low specific gravity, 2.58. It is almost exactly one-third as dense as iron and is about as light as glass and porcelain.

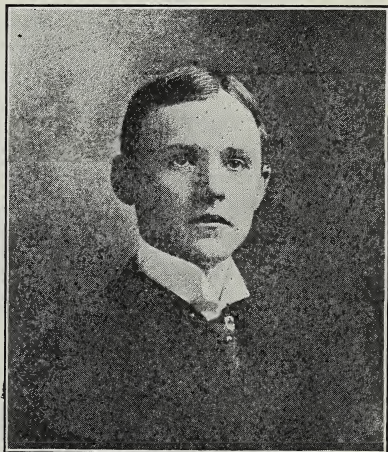


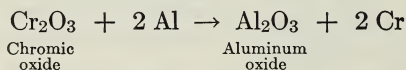
FIG. 213. CHARLES MARTIN HALL
(1863-1914).

American chemist and inventor; invented the electrolytic process for the extraction of aluminum and developed the American aluminum industry.

428. Chemical conduct. Melted aluminum absorbs oxygen and covers itself with a white layer of *aluminum oxide*, Al_2O_3 , which is ordinarily so thin as to be invisible. Powdered aluminum, made by shaking the melted metal in a closed box until it solidifies, burns with intense light display and has been used in flash-light powders. In the cold the metal is unaltered by dry air, and even moisture has only the effect of slightly dimming the lustre.

It will be recalled that the light metals in general oxidize rapidly in the air and energetically decompose water. The cause of the peculiar passiveness of aluminum toward air and water is the fact that *the aluminum oxide produced forms a thin, continuous film like a lacquer*, which protects the metal beneath and brings the oxidation to a standstill as soon as it begins. The true character of aluminum as a light metal, however, accounts for the fact that it cannot be prepared by the electrolysis of a solution of its compounds in water, for the newly deposited aluminum decomposes the water as rapidly as it is deposited.

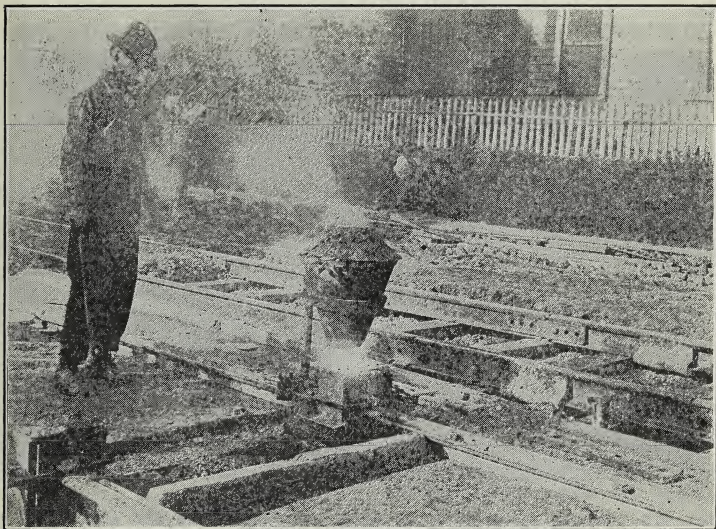
Granulated aluminum is a powerful *reducing agent*. Heated with an oxide of a metal, it combines with the oxygen and liberates the metal, producing an extremely high temperature. Chromium, for example, which is difficult to obtain by the usual methods, is easily prepared by the action of aluminum upon chromic oxide:



Aluminum is almost unaffected by nitric acid and by dilute sulphuric acid. Hydrochloric acid rapidly dissolves it.

429. Uses. Aluminum is used in making airplane and dirigible frames, automobile parts, electric conductors, cameras, drinking cups, soldiers' canteens, and other objects requiring strength combined with lightness. Because of the high con-

ductivity of aluminum for heat, cooking utensils made of it are economical of fuel. They are free from the sanitary objections attaching to vessels of copper. Their durability is unlimited if they are properly used, but they must not be cleansed with ammonia or with sodium carbonate or soap powders containing it, since these substances dissolve aluminum and would rapidly perforate the vessels.



Courtesy of the Metal & Thermal Corporation.

Fig. 214. The thermite reaction in progress for the bonding of a trolley rail.

Powdered aluminum is much used as a pigment for the radiators of heating systems. Aluminum leaf has displaced silver leaf for decorative purposes, and aluminum foil is as sanitary as tin foil and can be used instead of the latter for wrapping food products. The use of granulated aluminum for reducing the oxides of other metals is of great importance in preparing *chromium, manganese, molybdenum, titanium,* and other elements.

The powerful affinity of aluminum for oxygen is applied in the steel industry. A little aluminum added to melted steel in the ladle just before casting removes all oxygen from the steel and insures the formation of a sound ingot, free from blow-holes.

Of the *alloys* of aluminum, **magnalium** has been mentioned. Another useful alloy is **aluminum bronze**, which contains 90 per cent of copper and 10 per cent of aluminum. It has about

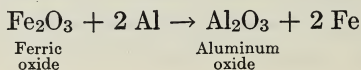


Courtesy of the Metal & Thermit Corporation.

Fig. 215. Broken sternpost of an Army transport before and after welding with half a ton of thermite-produced iron.

the color and lustre of gold, is hard, strong, easily cast, and permanent in the air. Cheap jewelry is often made of it, and it finds other important applications.

430. Thermite. When a mixture of granulated aluminum and oxide of iron is kindled by a special fuse, aluminum oxide and iron are produced:



The mixture, which is known commercially as **thermite**, is placed in a crucible lined with magnesia and ignited by means of a fuse supplied for the purpose. From the heated portion the chemical change spreads through the mass, which is carried to a temperature of $3,000^{\circ}$ by the large evolution of heat which takes place.

Thermite is used, not for the manufacture of iron, which can be made far more cheaply by other methods, but for producing high temperatures. Trolley rails and iron pipes are joined by means of it, broken shafts on steamships are welded without removal, and other local repairs to machinery are effected with a minimum of delay and expense.

In welding two sections of trolley rail the crucible is supported over the junction and the thermite ignited. After a few seconds the bottom of the crucible is suddenly perforated, and the white-hot iron flows over the joint and binds the two rails together. After cooling the excess of iron is removed from the weld by a grinding wheel operated by the trolley current.

COMPOUNDS OF ALUMINUM

431. Aluminum oxide, Al_2O_3 . Aluminum oxide, commonly called **alumina**, is the mineral **corundum**, which occurs in opaque or translucent masses, bluish-gray to brown in color. It can be distinguished from other minerals by its intense hardness, which nearly equals that of the diamond. **Emery** is impure corundum, colored black by oxides of iron. It is an important abrasive.

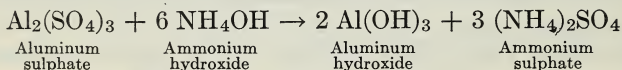
Ruby is transparent crystallized corundum, colored red by a trace of an oxide of chromium. "Scientific" rubies are made by melting a mixture of pure aluminum oxide with a trace of chromium oxide in the oxy-hydrogen flame or in an electric furnace. Natural and scientific rubies can be distinguished from glass imitations by their superior lustre, greater hardness, and higher specific gravity (4). To distinguish the natural

from the scientific ruby requires careful examination with the microscope. The finest rubies come from Burma, near Mandalay, where they occur in compact limestone or, less frequently, in soil and gravel.

Clear crystallized corundum colored blue by a trace of *titanium oxide* forms the **sapphire**, which is found in Ceylon, Australia, Montana, and elsewhere. The gem has been produced artificially, and the scientific sapphires are almost indistinguishable from the natural stones. The hardness and specific gravity of the sapphire are identical with those of the ruby. "*White sapphires*" consist of transparent aluminum oxide without coloring impurities.

Aluminum oxide can be made in the laboratory by heating the hydroxide to redness. Thus prepared, it is a white, amorphous powder, infusible in the Bunsen flame, insoluble in water, and scarcely affected by acids. It melts at $1,900^{\circ}$ to a glassy mass which is used under the name "**alundum**" as an abrasive and in making tubes and crucibles for chemical work requiring resistance to high temperatures.

432. Aluminum hydroxide, $\text{Al}(\text{OH})_3$. Aluminum hydroxide can be obtained as a gray, slimy precipitate by adding ammonium hydroxide to a solution of aluminum sulphate:



In purifying water by the rapid sand-filtration process, it is aluminum hydroxide that coats the grains of coarse sand with a slimy, gelatinous layer and makes of it an efficient filtering medium. The effect can be illustrated by adding to each of two glasses of water a pinch of clay or soil. Next add to one glass only a few drops of aluminum-sulphate solution, followed by a little calcium-hydroxide solution (lime water) to precipitate aluminum hydroxide. On standing, the water in this glass will become quite clear before that in the other shows any

subsidence worth mentioning. Any brown or yellow color that the water may possess, due to the presence of organic matter, will be removed at the same time.

This decolorizing action of aluminum hydroxide can be shown by treating a dilute solution of litmus with aluminum-sulphate solution and lime water. The liquid becomes colorless, while the aluminum hydroxide which settles to the bottom acquires a blue color. Solutions of many other dyes yield up their dissolved coloring matter to aluminum hydroxide in the same way. The colored compounds that are formed when aluminum hydroxide is precipitated in a solution containing dyestuffs are called **lakes** and are used as pigments.

433. Mordants. The power of aluminum hydroxide to absorb dyestuffs is widely used in the textile industry. Many dyestuffs will not color cotton and linen. If, however, the fabric be impregnated with aluminum hydroxide before being placed in the dye bath, then a lake is formed, and the same dyestuffs yield beautiful shades, especially fast both to light and soap. The impregnation of the cotton or linen fabric with aluminum hydroxide may be accomplished by digesting the goods first in a solution of aluminum sulphate and then in dilute ammonium hydroxide.

A substance that, though not a dyestuff itself, possesses this power to fasten the coloring matter to the fibre is called a **mordant**. Other insoluble hydroxides, especially those of antimony, chromium, iron, and tin, are used as mordants. With two different mordants the same dye often yields two lakes which differ completely in shade. For instance, the important coal-tar dye *alizarin* gives a brilliant red on goods mordanted with aluminum hydroxide but produces a dark purple when the fabric is impregnated with iron hydroxide, $\text{Fe}(\text{OH})_3$. Thus, by proper printing of the mordants on the goods, two or more colors can be obtained from the same dye bath, while those portions of the cloth that were not mordanted at all remain white.

434. Aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3$. The important salt *aluminum sulphate* is made by boiling bauxite with sulphuric acid in a lead-lined cauldron and pouring out the resulting solution into a large shallow tray in which it is allowed to solidify to a colorless, crystalline cake.

Aluminum sulphate forms colorless imperfect crystals, very soluble in water, the composition of which corresponds to the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$. It is the cheapest soluble compound of aluminum and is used extensively in the purification of public water supplies, as a mordant in dyeing, in waterproofing cloth, in sizing paper, and in the manufacture of alum.

435. The alums. Ordinary **alum** is a compound of 1 molecule of potassium sulphate, K_2SO_4 , with 1 of aluminum sulphate. It also contains 24 molecules of water, so that the composition corresponds to the formula $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$. This is often simplified by dividing through by 2. Written in this way, the formula becomes $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$.

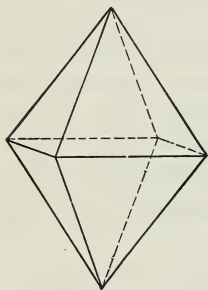


Fig. 216. The octohedral form of the alum crystal.

Alum is made by mixing solutions of potassium sulphate and aluminum sulphate and allowing the alum formed to crystallize on strips of lead, which are hung in the vessel.

Alum forms colorless octahedral crystals (Fig. 216), which dissolve in 7 times their weight of water at room temperature and in less than one-third their weight of boiling water. It is used in tanning glove kid, in making one variety of baking powder, in photography, and at times in the household as an addition to pickles and other food products. Alum is more easily purified than aluminum sulphate, and it is often used instead of the latter in mordanting delicate shades of red, which would be darkened and spoiled by the traces of iron that aluminum sulphate usually contains.

Alum is really the name of a *class* of double sulphates. In the formula $\text{KAl}(\text{SO}_4)_2$, the place of the K may be taken by other *univalent* metals and radicals, like Na and NH_4 . Moreover, the place of the Al may be taken by other *trivalent* metals like chromium (Cr) and iron (Fe). Hence the alums are quite numerous. Three of them which are of considerable practical importance may be mentioned:

Ammonium alum, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, resembles potassium alum closely but is cheaper. For this reason ammonium alum is displacing the potassium compound for many purposes.

Sodium alum, $\text{NaAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, is colorless and more soluble in water than potassium alum. Owing to its cheapness, sodium alum is becoming an important commercial product.

Chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, forms plum-colored octahedral crystals. It is added to the fixing bath in photography to toughen the gelatin film.

SUMMARY

The mineral *colemanite*, which is **calcium borate** and which is found abundantly in California and Nevada, serves in the United States as the raw material for the manufacture of the compounds of **boron**.

In a volcanic region in Italy, jets of steam charged with the vapor of **boric acid**, H_3BO_3 , issue from the rocks.

Boron is a gray solid about as hard as the diamond.

Boric acid, H_3BO_3 , has antiseptic properties and is used in toilet powders and (illegally) to prevent the decay of food products. Its solution in water is an excellent eye wash.

Borax forms white crystals which correspond to the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$.

Aluminum makes up nearly 8 per cent of the earth's crust. It occurs chiefly in silicates of aluminum with other metals.

Aluminum is made by the electrolysis of a solution of *aluminum oxide* in melted *cryolite*, Na_3AlF_6 .

Thermite is a mixture of granulated aluminum with iron oxide.

Aluminum oxide, Al_2O_3 , is the mineral *corundum*. **Emery** is impure corundum. The **ruby** and the **sapphire** are both composed of aluminum oxide colored by traces of impurities.

Aluminum hydroxide, $\text{Al}(\text{OH})_3$, is important in connection with the purification of water supplies. It has a remarkable affinity for dyestuffs, a property which is constantly applied in the textile industry.

A **mordant** is a compound that fastens the dyestuff to the fibre. Most mordants are compounds of *aluminum*, *antimony*, *chromium*, *iron*, or *tin*.

Aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3$, is the cheapest and most important soluble compound of aluminum.

Potassium alum is a double sulphate of the formula $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Since other univalent metals may take the place of the potassium and other trivalent metals that of the aluminum, the total number of alums is quite large.

EXERCISES

1. What is the difference between *aluminum* and *alumina*?
2. How does aluminum differ in chemical conduct from other light metals like sodium and potassium? Why?
3. What *gems* are composed of aluminum oxide? How can they be made artificially?
4. How can borax be made from colemanite? From boric acid?
5. What is a *mordant*? Explain how several colors can be produced by a single dye bath. What is a *lake*?
6. Calculate the percentage of *water* (a) in potassium alum; (b) in chrome alum.
7. Calculate the percentage composition of borax. Calculate *water*, not hydrogen and oxygen.
8. Calculate the percentage composition of cryolite.
9. What is the difference between *borax* and *borax glass*? How does borax behave when heated in the Bunsen flame? Why?

10. Aluminum is the most abundant metallic element in nature. Why is it not the cheapest?
11. Why is the plant for producing aluminum always located near a source of water power?
12. A solution of borax turns *red* litmus *blue*, whereas a solution of aluminum sulphate turns *blue* litmus *red*. Why?
13. Aluminum kitchen utensils are somewhat expensive. Why are they so widely used?
14. Under what conditions would thermite welding be chosen in preference to the ordinary methods?
15. How could you distinguish a white sapphire from a diamond?
16. Aluminum chloride, AlCl_3 , is a white solid which dissolves in many liquids. The water solution is acid to litmus but the other solutions are not. Explain.

REVIEW QUESTIONS

1. Explain the meaning of the term *hydrolysis*.
2. Make a list of the industrial processes thus far studied that you would expect to find located near Niagara Falls.
3. What is an *abrasive*? What abrasives have been studied up to this point?

CHAPTER XXXIV

GROUP IVA. THE CARBON FAMILY

CARBON, SILICON

436. General. Carbon has already been studied. The elements of Group IV, which includes the Carbon Family (carbon, silicon) and the Tin Family (tin, lead), are found chiefly in their compounds, silicon being by far the most abundant. Carbon and silicon are *non-metals*, while tin and lead are *metals*. Carbon and silicon are *quadrivalent*. Tin and lead are *quadrivalent* in some compounds, but in their most familiar and important salts they are *bivalent*.

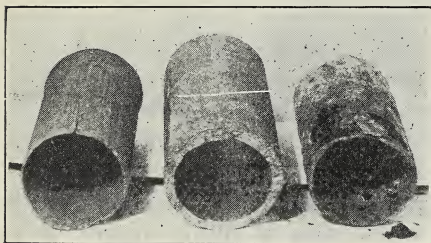
SILICON (Si = 28)

437. Occurrence. In abundance silicon stands next to oxygen, making up 28 per cent of the solid crust of the earth. *Silicon dioxide*, SiO_2 , is **quartz**, the most abundant of minerals. Enormous quantities of silicon occur also in the form of various *silicates*, some of which are rock-forming minerals of great importance.

Feldspar, *mica*, and *clay* have already been mentioned. The abundant mineral **hornblende** is *calcium silicate*, CaSiO_3 . It frequently contains magnesium and iron also. **Asbestos** is a fibrous variety of hornblende. **Serpentine**, **talc**, **soapstone**, and **meerschaum** are all silicates of magnesium containing water. Volcanic *lava* is composed of silicates. Common rocks like *granite*, *basalt*, *trap*, *porphyry*, *sandstone*, and *slate* consist wholly of silicates and quartz. Limestone is, in fact, the only abundant rock that is not made up of compounds of silicon.

wireless telegraphy. It has been employed in cast acid-proof vessels for the chemical industry. Its most important application is as an addition to melted steel before casting, wherein it acts in the same way as does aluminum, deoxidizing the liquid steel and giving a sound casting, free from blowholes.

439. Ferro-silicon. When a mixture of sand and coke with scrap iron or iron ore is melted in an electric furnace, an alloy of iron and silicon, known as **ferro-silicon**, is obtained. Accord-



Courtesy of the Durtron Castings Co.

Fig. 217. Acid-resisting power of iron high in silicon.

The middle pipe of duriron was practically unaffected by immersion in 10 per cent nitric acid for 360 hours and 10 per cent sulphuric acid for 360 hours. The two cast-iron pipes were originally of the same length and thickness as the duriron pipe. The one on the left was immersed in 10 per cent nitric acid for 160 hours, and the one on the right in 10 per cent sulphuric acid for 240 hours.

ing to the proportions taken in the charge, the product may contain from 20 per cent to 70 per cent of silicon, the balance being iron and carbon. The usual grade averages about 50 per cent of silicon.

Ferro-silicon is widely used in the steel industry for deoxidizing melted steel before casting and for making steel and iron high in silicon for special purposes. In transporting ferrosilicon, especially by water,

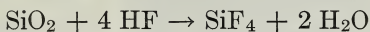
it is necessary to remember that when wet, or when in contact with damp air, it may give off highly poisonous gases. Fatal accidents have occurred on shipboard from this cause.

Acid-proof iron, which is sold under the trade names of "**duriron**" and "**tantiron**," is cast iron containing 15 per cent of silicon. Metal of this composition is scarcely affected by nitric or sulphuric acid. By a further increase in the percentage of silicon the iron can even be made to withstand the action of hydrochloric acid. For handling acids on a large

scale, acid-proof iron is displacing glass, porcelain, and stoneware, over which it has the great advantages of greater strength and better conductivity for heat.

COMPOUNDS OF SILICON

440. Silicon dioxide, SiO_2 . Silicon dioxide, often called **silica**, can be obtained artificially as a white powder, which melts only at a very high temperature and is insoluble in water and in the ordinary acids. *Hydrofluoric acid*, HF , converts it into *silicon fluoride*, SiF_4 , which escapes as a gas:



Silica occurs in nature in many varieties as the abundant mineral **quartz**. Pure quartz, often called **rock crystal**, is found in colorless, glassy crystals which have the form of a hexagonal prism terminating in two hexagonal pyramids (Figs. 34 and 218). When cut and polished, rock crystal is used in inexpensive jewelry under the name of “**rhinestone**” or “**quartz diamond**.” Rock crystal colored violet by a trace of manganese is the semi-precious stone **amethyst**. A red variety of quartz forms the **carnelian**, and the **false topaz** is cut from transparent yellow quartz. **Aventurine** is quartz with glittering scales of mica or of ferric oxide disseminated through it.

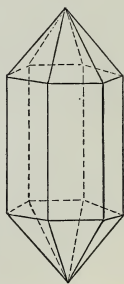
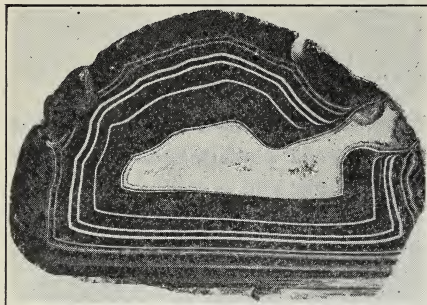


Fig. 218. Hexagonal form of quartz crystal.

Quartz also occurs in masses which possess no distinct crystalline form. **Flint** is massive quartz which readily breaks into fragments with sharp edges, and for this reason it was used for axes, knives, and arrow-heads before man learned how to extract the metals from their ores. **Jasper** is similar to flint, but possesses a yellow color which makes it suitable for ornamental purposes. **Agate** is quartz depos-

ited from water in wavy bands, differing in color, which give the stone, when cut and polished, an attractive appearance.



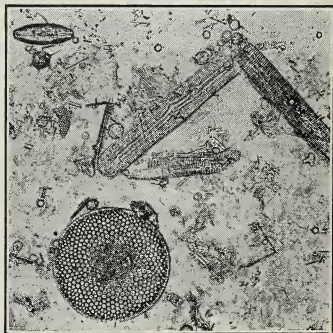
Courtesy of the U. S. National Museum.

Fig. 219. Agate.

Onyx is identical with agate except that the bands are straight. **Petrified wood** is the result of decaying wood under water containing dissolved silica. The silica replaces the decaying wood bit by bit, so that the structure of the original wood is preserved.

Silica is the chief constituent of *sand*, which, when pure-white and free from iron compounds, is in great demand for the manufacture of glass. *Soil* consists chiefly of sand and clay, mixed with decomposing vegetable matter called *humus*. The loose, porous, so-called "warm" soils contain only about 10 per cent of clay and are rich in sand; the "cold" soils, which are not very permeable to water and tend to bake into hard clods after ploughing, may contain as much as 20 per cent of clay.

441. Opal. Opal has nearly the same composition as quartz but is *amorphous*. It is also less pure, containing water and traces of ferric oxide in addition to the silica. **Infusorial earth** is a mass of microscopic shells of the family of marine organisms known as *diatoms*,



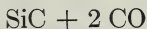
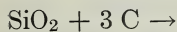
Courtesy of the Bureau of Mines.

Fig. 220. Diatoms in infusorial earth, enlarged 130 diameters.

consisting of opal. It is used in scouring powders and in the manufacture of dynamite (§ 605). When opal exhibits a beautiful play of colors, it is used as a gem under the name of "*precious opal*."

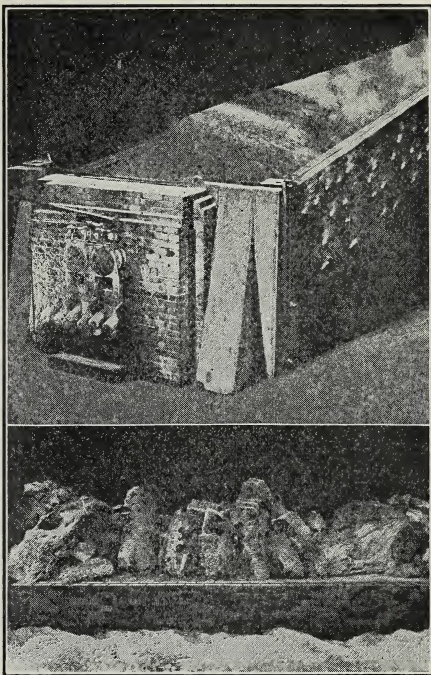
The finest opals come from Hungary, Mexico, Honduras, and Australia.

442. Silicon carbide, SiC. Silicon carbide, commonly called **carborundum**, is made by the action of carbon on silica at the temperature of the electric furnace:



The silica is used in the form of sand, and the carbon as coke. Some salt is added to the mixture to make it melt more readily, and some sawdust to make it porous. These materials are contained in a rectangular furnace,

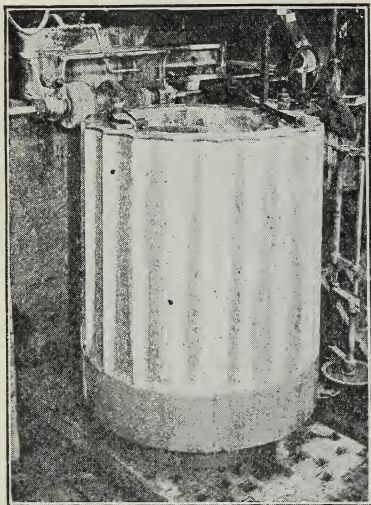
similar to the furnace for the manufacture of artificial graphite (Fig. 133), the sides of which are built of loosely laid bricks. Graphite electrodes project into the mass, and there is imbedded in the mixture a core of granulated coke reaching from one electrode to the other. This core, being a bad conductor, becomes intensely heated when the powerful current is turned on.



Courtesy of the Carborundum Co.

Fig. 221. Carborundum furnace in operation; below, the furnace opened, ready to unload.

The current passes for 36 hours, during which time the furnace absorbs 1,000 horse-power and makes 4 tons of carborundum. The coke core and the portions of the charge in contact with it are converted into artificial graphite. Around the core is found crystallized carborundum in a layer a foot or more thick. Outside of this is a mass of imperfectly transformed material which goes back into the furnace with the next charge.



Courtesy of Julius Wegner Machine Works.

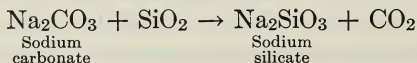
Fig. 222. Fluting a marble column with carborundum wheels.

When pure, carborundum forms beautiful colorless crystals, but the commercial product is black. It is harder than the ruby and almost as hard as the diamond, and all of its uses depend upon this fact. It finds extensive application as an abrasive, in making hones, grindstones, whetstones, and polishing paper. It is also used for the crown or cutting edge of rock drills.

THE SILICATE INDUSTRIES

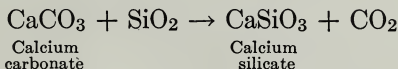
GLASS

443. Water glass. When silica, in the form of clean white sand, is melted with sodium carbonate, carbon dioxide escapes and sodium silicate remains:



Sodium silicate is a glassy mass, which is colorless when pure but is usually colored green by traces of iron silicate. Long boiling with water causes sodium silicate to dissolve and form a syrupy liquid. Hence it is called **water glass**. This solution is the form in which it is usually sold. It is employed for preserving eggs, for fireproofing wood and cloth, as a cement, and as an adulterant in cheap soaps.

444. Glass. Calcium carbonate, like sodium carbonate, when heated with silica, interacts with it, producing *calcium silicate* and carbon dioxide:

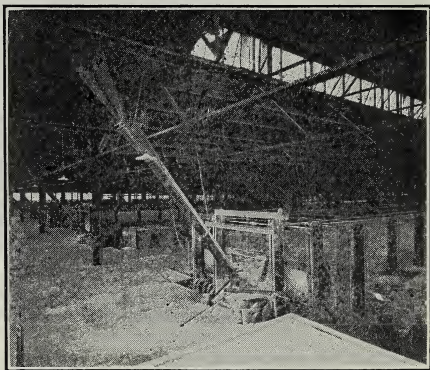


When a mixture of sodium carbonate and calcium carbonate is heated with silica, the product consists of *sodium calcium silicate*. This is ordinary **window or bottle glass**.

Glass is made by melting, in a large fire-clay tank, a mixture containing (1) silica in the form of clean white sand or crushed rock crystal; (2) sodium carbonate or sodium sulphate; and (3) some form of calcium carbonate, such as limestone, marble, or chalk.

Lime (CaO) is often used instead of calcium carbonate.

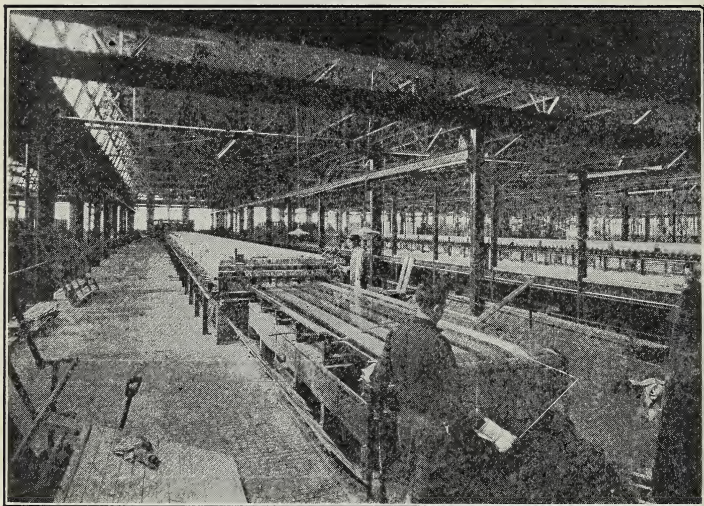
445. Lenses, prisms, lamp chimneys, and cut glass objects are made of **flint glass**. This is *potassium lead silicate*, made by melting sand and potassium carbonate with litharge (PbO) or red lead (Pb_3O_4) in covered fire-clay pots.



Courtesy of the Libbey-Owens Sheet Glass Co.

Fig. 223. A battery of glass tank furnaces.

The student will remember from his laboratory work that many compounds of the metals dissolve in beads of melted borax and produce characteristic colors on cooling. The same colors are obtained in glass by the same means. The **green** of ordinary bottle glass is due to *iron* compounds, while *iron* and *manganese* together produce a **brown** color. **Blue** glass is



Courtesy of the Libbey-Owens Sheet Glass Co.

Fig. 224. Modern machinery draws sheet glass without handling from the tank furnace to the finished sheet.

colored with *cobalt oxide*, and *manganese dioxide* yields an **amethyst** tint.

The “**paste**” which is used to imitate precious stones is lead silicate, made by melting pure sand with red lead. The appropriate colors are produced by adding compounds of the metals. The imitation sapphire is made by melting “paste” with a little cobalt oxide. The green color of the imitation emerald is produced by adding a little copper oxide and chro-

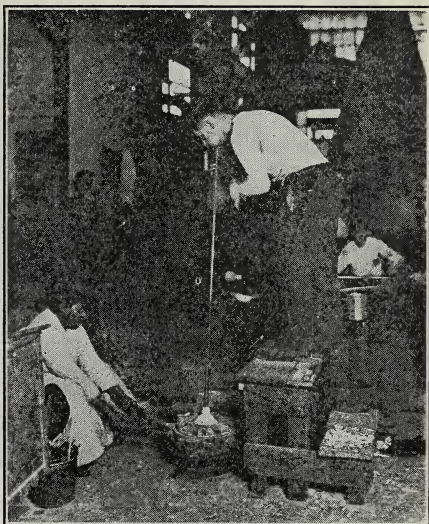
mium oxide to the paste. Imitation topaz is colored with gold, and imitation ruby with a mixture of manganese dioxide and gold. The "paste" without any coloring material serves to imitate the diamond. All these imitations are easily distinguished from the genuine minerals by the fact that the imitations are inferior in lustre and are much softer.

446. Opal glass, used for lamp shades and globes, is made by adding the powdered mineral *cryolite* to melted glass. The cryolite dissolves in the liquid glass, and when the glass solidifies, the cryolite separates in countless little crystals which render the glass translucent. *Fluorspar*, as we have already seen, can be used instead of cryolite.

Plate glass for mirrors and shop windows is made by pouring melted glass from a ladle on a cast-iron table with a raised rim. The glowing glass is smoothed at once with a heated iron roller and when cold is carefully polished.

Iridescent glass, which has a surface like mother of pearl, is obtained by heating the finished vessel under pressure with a 15-per cent solution of hydrochloric acid, which attacks the surface, producing a pearly film upon it.

The more silica a glass contains, the higher the temperature required to soften it and the better it resists the attack of chem-



Courtesy of the Ingersoll-Rand Co.

Fig. 225. Blowing an ornamental lamp shade in a mould.

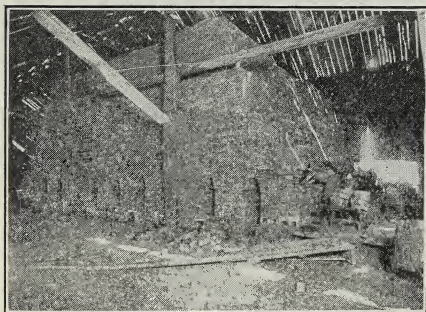
icals. Ordinary glass contains less than 70 per cent of silica, and "hard glass" more, up to 80 per cent.

Pure quartz, in the form of rock crystal or sand, can be melted at the high temperature of the electric furnace and worked into crucibles, tubes, beakers, and dishes. These vessels will bear the full heat of the Bunsen flame without softening, and they can be heated red-hot and then plunged into water without danger of breakage. They are unaffected by the ordinary acids. For these reasons vessels made of pure quartz are coming into extensive use in the chemical industries.

CERAMIC OR CLAY PRODUCTS

447. Clay. The pure white clay which is in such demand for the manufacture of porcelain and china is called **kaolin** by the mineralogist. It is aluminum silicate containing water, and its composition corresponds to the formula $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$.

Kneaded with water, clay forms a plastic mass which can be shaped at will into objects which become stone-hard when



Copyright, Brown Brothers.

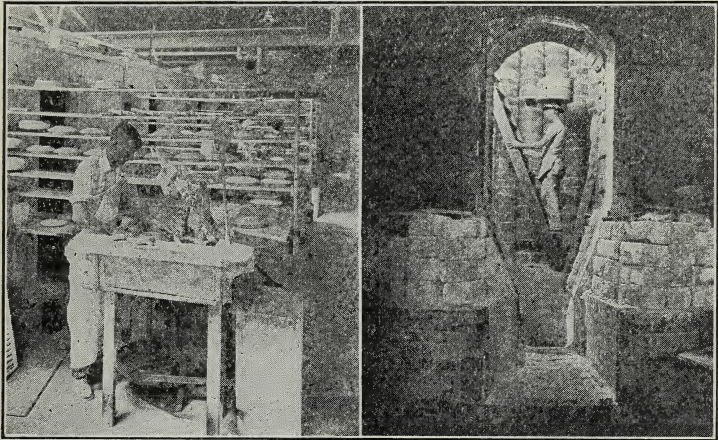
Fig. 226. Setting air-dried common brick for burning.

dried and heated short of fusion. When made of pure kaolin, these objects are white and remain white after being baked. In common clay the kaolin is colored by impurities which are chiefly compounds of iron, and vessels made of this impure clay turn red on being heated, because the iron during

the baking passes into the red compound *ferric oxide*, Fe_2O_3 . Upon the plasticity of wet clay and the hardening of the

plastic mass under the influence of heat is based the manufacture of bricks, terra cotta, tiles, porcelain, china, and all varieties of pottery.

448. Bricks are made of ordinary white or yellow clay, which is mixed with sand to prevent shrinkage during the heating. The red color of most bricks is due to the presence of ferric oxide. A brick is porous, for clay shrinks in the baking, and since the external shape and size are preserved, the mass acquires a spongy structure. **Pressed brick** is shaped in



Courtesy of Lenox, Incorporated.

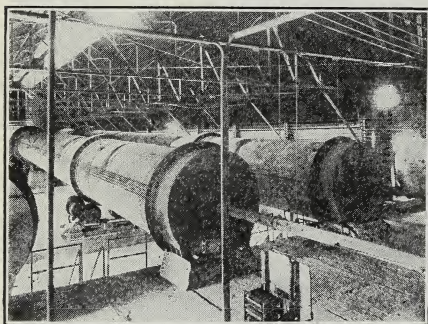
Fig. 227. Pottery making: left, moulding plates; right, loading the kiln with dishes packed in fire-clay boxes.

a mould and is compressed before baking by powerful hydraulic pressure.

An unglazed vessel of terra cotta, such as a flower pot, is like a brick except in shape. Terra-cotta vessels in which liquid is to be kept are **glazed**, that is, covered with a glassy film which is watertight. Glazing is often effected by throwing salt into the fire of the pottery kiln as the baking nears its end. The salt is vaporized, and its vapor interacts with the

clay and sand, forming a glassy layer of sodium aluminum silicate on the surface of the ware. Another method is to dip the vessel after baking into a creamy suspension of clay and lead oxide in water and then to bake again, when a glaze consisting of lead silicate is formed. The use of such a lead glaze on culinary utensils or on vessels intended to contain food products is objectionable.

449. Porcelain, or so-called "*real china*," is made of a mixture of 2 parts of pure white kaolin and 1 part each of quartz and feldspar, both of which are finely powdered. After thorough mixing, the mass is stored away wet for some months and is then shaped and fired at a red heat. When cold the



Courtesy of the International Cement Co.

Fig. 228. Rotary gas-fired cement kilns.

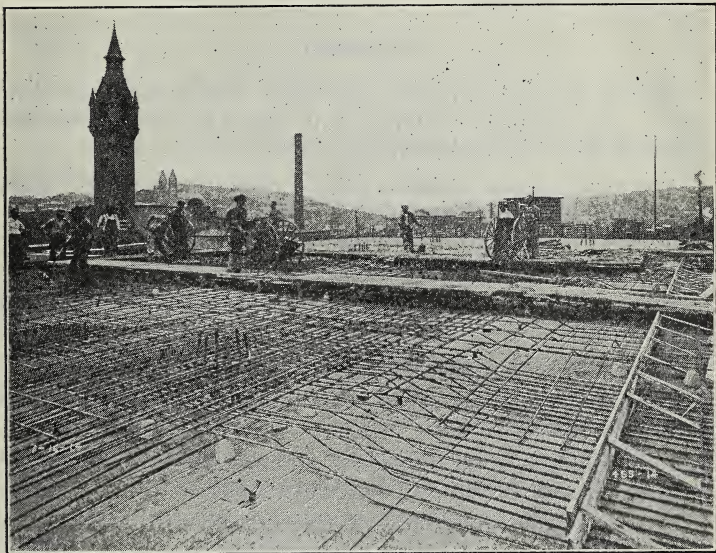
vessel is dipped in the glaze, which is a cream of finely powdered quartz, feldspar, marble, and kaolin suspended in water. The vessel is then fired again at a white heat, whereupon the glaze melts, partly fills the pores of the mass, and forms a hard, glassy film on the surface.

Common white ware, or "*stone china*," is made of white clay mixed with bone ash and is fired at a lower temperature than porcelain. The glaze is usually a lead glaze like that used on terra cotta, and the interior of the mass is quite porous.

On both "*stone china*" and "*real china*" the colored decorative work is done with specially prepared glasses colored with metallic oxides. The colored glasses are finely powdered, mixed with oil of turpentine, and painted on over the glaze, after the second firing. When the vessel is fired a third time, the new material melts into the glaze and becomes firmly

attached. Finely powdered gold and silver are mixed with turpentine and applied in the same way.

450. Cement. *Portland cement* is made by mixing clay with 3 times its weight of powdered limestone and heating the mixture almost to fusion in a rotary kiln (§ 381), from which it issues in the form of a mass of small semi-fused lumps known as



Courtesy of the Turner Construction Co.

Fig. 229. Pouring the roof of a reinforced-concrete building.

“clinker.” The clinker is then ground so fine that more than three-fourths of it will pass through a sieve having 200 meshes to the inch.

In use cement is mixed dry with twice its volume of sand, and the mixture is then transferred to a rotating drum called the “mixer.” Here the cement and sand are mixed with 4 times their joint volume of crushed stone or gravel and with water. This final product is called **concrete**. When allowed

to "set," it forms an artificial stone the hardness and strength of which slowly increase for years.

It is a fortunate fact that steel surrounded with concrete is protected against rust, even in the presence of moisture. For this reason twisted steel rods are widely used for increasing the strength of concrete walls. This type of construction is known as **reinforced concrete**.

SUMMARY

Silicon is a hard, brittle, gray solid, which does not occur native. In chemical combination it makes up more than one-fourth of the crust of the earth.

Quartz is **silicon dioxide**, SiO_2 . *Rock crystal, flint, agate, chalcedony, white sand, and petrified wood* have the same composition as quartz. The semi-precious stones *amethyst, aventurine, carnelian, and false topaz* are forms of quartz.

Ferro-silicon is an alloy of iron and silicon much used in the iron industry.

Acid-proof iron contains 15 per cent or more of silicon.

Opal is amorphous silica, containing small quantities of water and ferric oxide.

Carborundum is an important abrasive made by heating a mixture of coke and sand in an electric furnace.

Silicates are compounds of the metals with silicon and oxygen. They are abundant rock-forming minerals. Among the great industries based on the silicates are the manufacture of *bricks, tiles, terra cotta, pottery, glass, porcelain, and cement*.

EXERCISES

1. Explain the distinction between *silicon* and *silica*.
2. Mention some of the more important forms in which silica occurs in nature.
3. What is a *silicate*? Mention some rock-forming silicates.
4. Describe the manufacture of glass. What is the difference between *hard* and *soft* glass? What is *flint glass*? *Paste*? *Quartz glass*?

5. What effect has the percentage of clay upon the properties of a soil?
6. Describe the manufacture of terra cotta, porcelain, and stone china.
7. How is Portland cement prepared? What is *concrete*?
8. What is *carborundum* and how is it made?
9. Calculate the percentage of silicon (*a*) in quartz, (*b*) in pure clay, (*c*) in asbestos.
10. How many kilograms of solid water glass can be made by melting 1,000 kg. of sand containing 90 per cent of silica with sodium carbonate?
11. Why is sodium silicate called "water glass"? Mention some of its uses.
12. Either silicon or carborundum can be made by heating coke with sand. Explain, using the equations.
13. The chemist often has occasion to fuse minerals with sodium carbonate. Would you make this fusion in a crucible of quartz glass or in one of platinum?
14. Water-glass solution is strongly alkaline to litmus. What do you conclude from this fact?
15. Ordinary sand and clay are very likely to contain small quantities of iron compounds. How would the manufacturer of glass and porcelain look upon this impurity in his raw material?
16. What is the difference between *quartz* and *opal*?

CHAPTER XXXV

GROUP IV B. THE TIN FAMILY

TIN, LEAD

Tin and lead, the two metals of the Tin Family, as we have seen in the preceding chapter, are *quadrivalent* in some compounds, but in their most familiar and important salts they are *bivalent*.

TIN (Sn = 119)

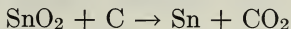
451. Occurrence. The tin of the world is obtained entirely from the mineral **cassiterite**, which is *stannic oxide*, SnO_2 , called by the miners **tinstone**. Tinstone can be distinguished from most other minerals by its dark-brown color, by its high specific gravity (7), which is more than double that of the common rocks, and by its hardness, which is so great that tinstone scratches glass when drawn over the surface of the latter.

Tinstone is found in Cornwall, England, in the Malay Peninsula and the neighboring islands, especially Banka and Billiton, and in Bolivia. No deposits of importance are known in the United States.

In Cornwall and elsewhere cassiterite occurs as gravel in the beds of streams, and this form of tin ore is known as "*stream tin*." Owing to its high density, the stream tin can be cheaply separated from other pebbles which occur with it by merely washing with a regulated current of water; the lighter pebbles are carried away and the stream tin remains.

452. Metallurgy. To extract the tin, tinstone is pounded in a stamp mill to a powder, which is washed in a current of water to remove impurities of lower specific gravity. It is then

dried, mixed with one-eighth of its weight of powdered coal, and heated to redness in a reverberatory furnace (Fig. 230), the doors of which are kept closed to exclude oxygen. At a red heat the stannic oxide is rapidly reduced by the carbon:



And the melted tin collects on the hearth of the furnace, from which it is drawn off into moulds when the reduction is complete.

The chief impurities in the crude tin are iron, copper, antimony, and arsenic. For purification advantage is taken of the fact that the melting point of tin (232°) is much lower than that of the impurities found in it. The

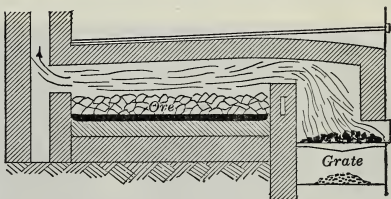


Fig. 230. Reverberatory furnace.

bars of tin are piled in a furnace and carefully heated. When the temperature reaches 232° , the tin melts and runs out. The remaining impurities are removed by stirring the melted tin with wet wooden poles, whereupon the escaping steam carries the dross to the surface where it can be skimmed off.

453. Properties. Tin is a white, lustrous metal resembling silver in appearance, but its specific gravity (7.3) is much less than that of silver, and it melts far more easily.

Tin is harder than lead but not so hard as zinc. It is quite malleable and is readily beaten or rolled into foil, but it has little tenacity and can hardly be drawn into wire. When exposed to cold, tin gradually passes into another allotropic modification, which is a loose gray powder known as **gray tin**. The change is so slow that years may be required before it is complete. Warming the gray tin reconverts it at once into the familiar white metal.

454. Chemical conduct. Tin is scarcely affected by water and air in the cold—hence its use for protecting iron against

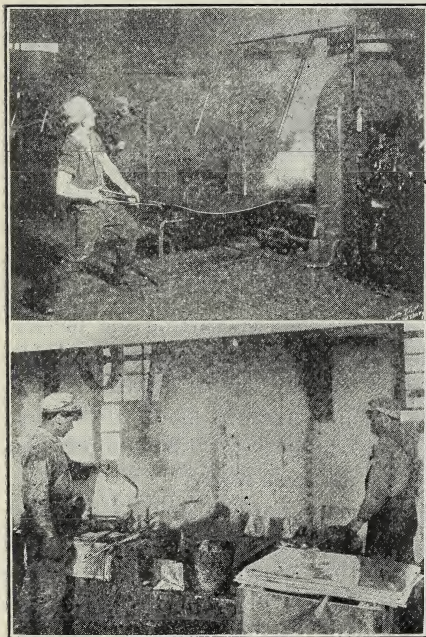
rust. At high temperatures melted tin absorbs oxygen and slowly passes into a white powder of *stannic oxide*, SnO_2 .

Tin dissolves in concentrated hydrochloric acid, which changes it into *stannous chloride*, SnCl_2 . Nitric acid rapidly converts it into a white, insoluble powder which consists of stannic oxide and water.

455. Uses. Tin foil, which is made by hammering or rolling the purest grade of bar tin, is largely used for wrapping tobacco and food products. The tin vessels of the household are made of soft sheet steel and are then carefully cleaned and dipped into melted tin. After cooling the vessel may be dipped a second, and even a third and fourth, time in the preparation of high-grade ware. Tin plate is made in the same way.

In using tin vessels it should be remembered that they must not be exposed to temperatures above 232° . They answer excellently for boiling or stewing, but if they are employed for frying, broiling, or baking, the tin may melt and mix with the food.

For roofing, sheet steel is often coated with an alloy of tin and lead. The product is known in trade as "**terne plate.**"



Courtesy of the Philadelphia Commercial Museum.

Fig. 231. Hot-rolling (above) and dipping (below) sheet iron for the manufacture of tin plate.

Because of the marked poisonous action of lead, *terne* plate is not used in making cooking utensils.

Tin compounds have little ill effect upon the body. For this reason the interior of copper stewpans is often coated with tin. This is done by pouring a little melted tin into the vessel, adding a small quantity of powdered rosin, and rubbing the tin over the copper until the coating seems satisfactory. The harmlessness of tin compounds explains the enormous use of cans made of tin plate for preserving food products.

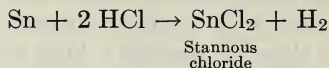
456. Alloys of tin. **Bronze** and **gun metal**, which are alloys of tin and copper, have been mentioned under the latter metal. Plumber's **solder** is made by melting 1 part by weight of tin with 2 parts of lead. **Pewter** contains 80 per cent of tin, the remainder being lead. **Britannia metal** contains 90 per cent of tin, to which are added 8 per cent of antimony and 2 per cent of copper to increase the hardness of the alloy.

Among the most useful of all metals are the **bearing metals** so essential in the bearings of locomotives and machinery of all sorts. They consist chiefly of tin and lead, hardened by small percentages of antimony and copper. **Babbitt metal** is the most important of these alloys. It contains 35 per cent of tin, 50 per cent of lead, 13 per cent of antimony, and 2 per cent of copper. The **fusible alloys** employed in automatic fire-protection apparatus and for fuses in electric circuits are alloys of tin with lead, bismuth, and other metals.

COMPOUNDS OF TIN

457. Stannic oxide, SnO_2 . Stannic oxide, also called *tin dioxide*, is the **tinstone** of nature. Prepared by the oxidation of tin, it forms a dense, white, insoluble powder, which is largely used in glazing pottery and as a constituent of the enamel applied to "agate" cooking utensils.

458. Stannous chloride, SnCl_2 . *Stannous* chloride is made by dissolving tin in concentrated hydrochloric acid:



When the solution cools, white needles of the formula $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ are deposited, which are sold under the name of “tin salts” or “tin crystals” and are widely used as a mordant by the dyer and calico printer.

459. Stannic chloride, SnCl_4 . *Stannic* chloride is obtained as a product of the utilization of the cuttings of tin plate discarded in the manufacture of cans. These cuttings, which contain 3 per cent of tin, are compressed into a compact mass and packed into an iron cylinder into which dry chlorine gas is introduced. Heat is evolved, and the tin is converted into stannic chloride, which leaves the cylinder as a vapor and is condensed to a liquid by cooling. The iron remains unaffected and is sold as “scrap iron” to the steel maker. Old tin cans, after cleaning, are “detinned” in the same way.

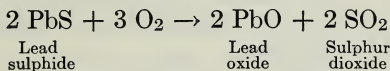
Stannic chloride is a dense, colorless, fuming liquid, which is used as a mordant and for weighting silk. Cotton goods soaked in a solution of stannic chloride and then in a solution of ammonium sulphate become fire-proof, even after many washings. Stannic chloride was used in hand grenades during the World War.

LEAD ($\text{Pb} = 207$)

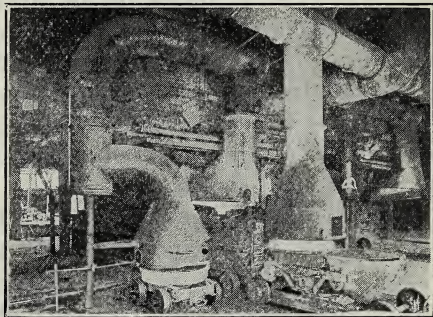
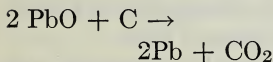
460. Occurrence. The chief ore of lead is the mineral **galenite**, which is *lead sulphide*, PbS . It is often called **galena** or **lead glance**. Galenite can easily be distinguished from other minerals by its lead-gray metallic lustre, by its high specific gravity (7.5), and by its cubical crystallization (Fig. 34), which is accompanied by a remarkable tendency to break into cubical fragments when struck with a hammer. Great deposits of

galenite exist in Illinois, Iowa, Missouri, and Wisconsin. It is also mined in Spain, England, Australia, and elsewhere.

461. Metallurgy. In extracting the lead from galenite the ore is mixed with 10 per cent of its weight of lime and thoroughly roasted in a reverberatory furnace at a gentle heat. This converts the lead sulphide into lead oxide, the lime acting as a catalyst:



The lead oxide is then mixed with coke and charged into a small blast furnace 20 ft. high and 3 ft. wide. A little iron ore and silica are also added to form a slag. A blast of air enters the bottom of the furnace through tubes called *tuyères*, which pass through the walls. At a low red heat the carbon of the coke reduces the lead oxide:



Courtesy of the National Lead Co.

Fig. 232. Lead blast furnace with forehearth and tapping ladles.

Melted lead collects in the bottom of the furnace and is tapped off from time to time.

The crude lead obtained in this way may contain silver, copper, arsenic, antimony, and other metals. The extraction of silver from lead has already been discussed (§ 350). The other impurities can be most cheaply removed by *oxidation*. The lead is melted in a furnace where a gentle current of air is drawn over its surface. The other metals oxidize before the lead, and their oxides rise to the surface and are removed by skimming.

462. Physical properties. Lead is a gray, lustrous metal. Its specific gravity is 11.4, and it is therefore noticeably heavier than the other base metals, though scarcely more than half as dense as gold and platinum. It is malleable and is readily rolled into sheet and foil, but it is not as tough as the other heavy metals, and it cannot be drawn into fine wire. The melting point of lead (327°) is lower than that of any other familiar metal with the exception of tin. Lead boils at $1,525^{\circ}$, which is a bright white heat.

463. Chemical conduct. Lead is less active than the other familiar base metals. Melted lead slowly absorbs oxygen and covers itself with a yellow scum of lead oxide, PbO . In the cold the brilliant surface of the freshly cut metal is rapidly obscured by a dark tarnish of oxide, but the attack is only superficial. Moist air converts lead into a white powder known as "**white lead**," which contains lead hydroxide and lead carbonate and has the formula $\text{Pb(OH)}_2 \cdot 2 \text{PbCO}_3$. The change is very slow, and for constructive purposes lead may be regarded as permanent in the air.

Hydrochloric acid slowly converts lead into white needles of *lead chloride*, PbCl_2 , and nitric acid dissolves the metal more rapidly to a solution of *lead nitrate*, $\text{Pb(NO}_3)_2$. Dilute sulphuric acid does not affect lead, but concentrated sulphuric acid slowly changes it into white *lead sulphate*, PbSO_4 .

464. Effect of lead on the body. Lead compounds are poisonous, and the poisonous effects are *cumulative*. This means that small quantities of lead absorbed daily accumulate in the system until dangerous or fatal results are produced. Among the symptoms of lead poisoning are a bluish line around the borders of the gums, a paralysis of the muscles that operate the wrist, and obstinate pains in the abdomen ("painters' colic"). Painters, grinders of pigments, type foundrymen, and, in fact, all workmen who deal with lead or its compounds are exposed to the danger of lead poisoning. It seems to be due chiefly to inhaling dust containing lead, and the danger can be

greatly reduced by ventilation and by avoiding the formation of dust by grinding lead compounds *wet*.

465. Uses. The softness of lead and its lack of tenacity prevent it from competing with iron and copper in structural work. On the other hand, it is, with the exception of iron, the cheapest of the metals, and its resistance to the weather and to the action of sulphuric acid and many other chemicals renders it one of the most important constructive materials of the chemical engineer. The chambers in which sulphuric acid is manufactured are made of lead, and tanks, vats, kettles, and pipes lined with lead are employed in many processes in which sulphuric acid is used. Lead pipe is largely used for sheathing underground cables, but for the water connections of the household iron pipe has taken the place of the lead pipe formerly employed. Shot is cast from lead containing 2 per cent of arsenic, which is added to increase the hardness. The final polish is put upon the shot by agitating them in a rotating drum with a little graphite. One-third of the total output of lead is made into pigments for the paint industry.

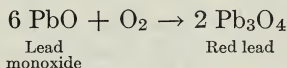
466. Alloys of lead. The *bearing metals* and *fusible metals* which have already been mentioned are important lead alloys. **Hard lead** is lead alloyed with more or less antimony, which hardens the metal and increases its strength. The "compo-tube" of the plumber is made of hard lead. The bullets used in *shrapnel shells* are composed of hard lead containing 20 per cent of antimony. **Type metal** is an alloy of 70 per cent lead, 20 per cent antimony, and 10 per cent tin.

COMPOUNDS OF LEAD

467. Lead monoxide, PbO. Lead monoxide is made by oxidizing melted lead in a cast-iron drum which rotates on a horizontal axis. Shelves attached to the inner walls pick up the lead as the drum rotates and let it fall in thin streams. This quickens the oxidation by exposing a large surface of melted

lead to a current of air which is forced through the drum by a fan. Lead monoxide is also obtained as a by-product of the cupellation of lead containing silver (§ 350). It occurs in commerce as a dense pale-yellow powder, sold under the name **massicot**, or as a mass of yellow crystalline scales called **litharge**. Lead monoxide is used in the manufacture of flint glass (§ 445), in glazing pottery, as a pigment, in making varnish, and in the preparation of other lead compounds, especially of "red lead." A mixture of lead monoxide and glycerine makes an excellent cement for many household purposes.

468. Red lead, Pb_3O_4 . Red lead, also called **minium**, is made by heating massicot to 300° in a current of air:



Red lead is a bright-red powder which is widely employed as a pigment, especially as a first coat to protect structural steel against rust. It is also used in making flint glass and as one constituent of the heads of matches. Mixed with linseed oil, red lead is employed as a "lute" or cement to make joints tight in gas fitting.

469. Lead dioxide, PbO_2 . Lead dioxide is a dense brown powder, which is of great importance as the chief constituent of the positive plates of storage batteries.

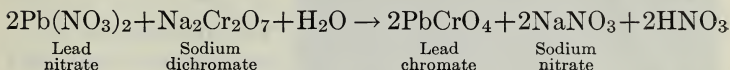
Most of the compounds of lead are insoluble in water. The most important soluble salts are *lead nitrate* and *lead acetate*.

470. Lead nitrate, $\text{Pb}(\text{NO}_3)_2$. Lead nitrate is prepared by dissolving lead in nitric acid. When the solution is evaporated and allowed to cool, lead nitrate separates in colorless crystals, which are freely soluble in water.

471. Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. Lead acetate, because of its sweet taste, is called "**sugar of lead**." It is made by dissolving litharge in acetic acid. It forms white crystals which correspond to the formula $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$. Lead

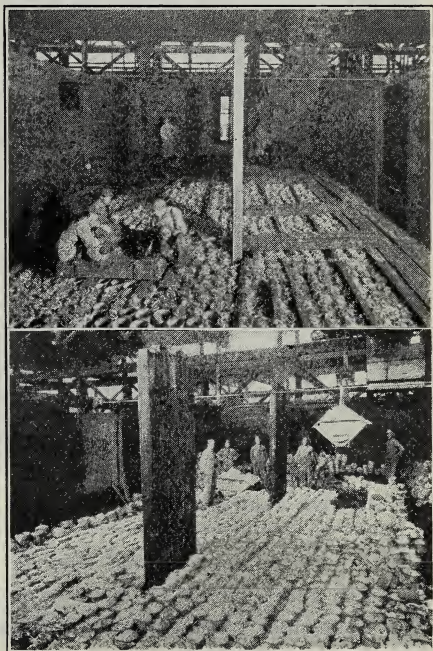
acetate is poisonous. Its solution is employed externally in the treatment of sprains, bruises, and ivy poison.

472. Lead chromate, PbCrO_4 . Lead chromate is the important pigment **chrome yellow**. It is made on a large scale by mixing a solution of lead nitrate with a solution of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$:



The lead chromate separates as a dense, bright-yellow precipitate, which is collected by filtering the liquid through canvas, removed from the canvas by scraping, and ground in linseed oil for use. It is quite poisonous and should not be used in coloring paper intended for wrapping food products.

473. White lead, $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$. One-fifth of the world's production of lead is consumed in the manufacture of the important pigment **white lead**, which is made by several different methods. The *Dutch process*, though tedious, yields a pigment



Courtesy of the Eagle-Picher Lead Co.

Fig. 233. Making white lead by the Dutch process: above, setting the "stack"; below, the stack after 90 days.

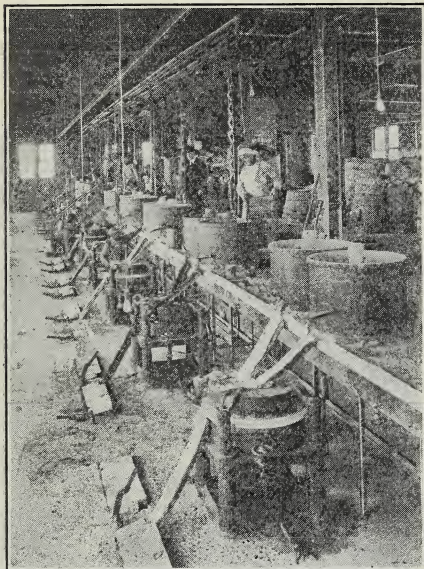
The *Dutch process*, though tedious, yields a pigment

of unsurpassed smoothness and covering power and is largely worked in the United States and England.

In this process a little acetic acid ($C_2H_4O_2$) is placed in the bottom of an earthen pot, which is then filled with perforated disks of lead. A number of such pots are placed in moist

tanbark on the floor of a shed and covered with planks upon which are placed another layer of tanbark and a second series of pots, and so on until the roof of the shed is reached.

The rotting of the bark warms the pots gently and serves as a source of carbon dioxide. The acetic acid slowly attacks the lead, and the carbon dioxide converts the lead acetate thus formed into white lead. After 4 months the lead disks are almost completely changed to white lead, which is ground wet,



Courtesy of the Sherwin-Williams Co.

Fig. 234. Paint grinding and mixing.

mixed with linseed oil, and sold as a paste. In making this pigment great care is required to avoid the constant danger of lead poisoning. For this reason the manufacture of white lead is forbidden in France.

474. Paints. Linseed oil, when spread out in a thin layer on wood, gradually oxidizes and hardens to a tough, elastic film which adheres firmly to the wood. The hardening is especially rapid and complete if the oil is boiled before use.

This fact is the basis of the manufacture of paint and of oil varnish. White paint is made by mixing white lead with linseed oil and thinning the mass with turpentine until it works well under the painter's brush. To accelerate the hardening of the paint it is usual to add a small quantity of a liquid called the *dryer*, which is made by boiling linseed oil with litharge or with manganese dioxide.

White lead is expensive and poisonous, and therefore it is often partly replaced by other white pigments, such as zinc oxide, lithopone, (§ 407), kaolin (§ 447), or barium sulphate (§ 392). This is especially true of inside work, for which white lead is now rarely used. Colored paints contain, in addition to these constituents, the *colored* pigment, for instance, chrome yellow for yellow paints, red lead or vermilion for red paints, etc.

SUMMARY

The only **ore of tin** is the mineral *cassiterite*, which is **stannic oxide**, SnO_2 . It is reduced to tin by heating to redness with powdered coal.

Tin foil is used for wrapping food products. **Bronze**, **gun metal**, **Britannia metal**, **Babbitt metal**, **pewter**, and **solder** are *alloys* of tin. The largest use of tin is for *plating iron*.

The most important compounds of tin are **stannous chloride**, SnCl_2 , **stannic chloride**, SnCl_4 , and **stannic oxide**, SnO_2 .

The chief **ore of lead** is *galenite*, or *galena*, which is **lead sulphide**, PbS . To extract the lead the galenite is roasted to *lead monoxide*, PbO , which is then reduced by heating with coke.

Lead is the densest, the least active, and, with the exception of iron, the cheapest of the useful base metals. Lead and its compounds are *cumulative poisons*.

The most important lead compounds are **lead monoxide**, PbO ; **red lead**, Pb_3O_4 ; **lead nitrate**, $\text{Pb}(\text{NO}_3)_2$; **lead acetate**, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$; **white lead**, $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$; and "**chrome yellow**" or **lead chromate**, PbCrO_4 .

Paint is made by suspending pigment in a mixture of linseed oil with turpentine and a little dryer.

EXERCISES

1. In an ice-cream freezer the rotating mechanism is made of galvanized iron, but the can that contains the cream to be frozen is tin plate. Why?

2. What is the cause of the tendency of zinc white to displace white lead in paint?

3. Lead sulphate is insoluble in water. Could a solution of lead nitrate be used in testing for sulphates if barium chloride were not at hand? What other sulphates are insoluble in water, or nearly so?

4. Why is tin foil used instead of lead foil for wrapping chocolate and other food products?

5. What are the merits and disadvantages of tin as a coating for culinary utensils?

6. What are the causes of the importance of lead to the chemical engineer?

7. I have 100 tons of tin ore containing 3 per cent of stannic oxide. How could the stannic oxide be separated from the associated rock? How could the tin be extracted from the stannic oxide? How could the crude tin be purified? How many tons of pure tin would be obtained, assuming that 5 per cent of the tin originally present was lost during the extraction?

8. How many grams of tin and how many grams of a 30-per cent solution of hydrochloric acid are needed to prepare 100 grams of crystallized stannous chloride, $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$?

9. Calculate the percentage composition of stannic oxide.

10. Calculate the percentage of lead in (a) lead sulphide, PbS ; (b) lead sulphate, PbSO_4 .

11. How many grams of litharge can be made by oxidizing 40.5 grams of lead, and how many liters of oxygen, measured at 0° and 760 mm., would be absorbed?

12. Calculate the percentage composition of chrome yellow.

REVIEW QUESTIONS

1. What is the *electromotive series*? Why does galvanized iron stand up better when exposed to the weather than does tin plate?
2. What is a *mordant*? Make a list of substances thus far studied that are used as mordants.
3. Lead is much denser than are the other useful base metals. Is this a merit or a disadvantage for constructive work? Mention one use of lead for which its high specific gravity is an advantage.
4. Explain completely and with precision the meaning of the following statement: "The specific gravity of lead is 11.4, and its atomic weight is 207."

CHAPTER XXXVI

GROUP V. THE NITROGEN FAMILY

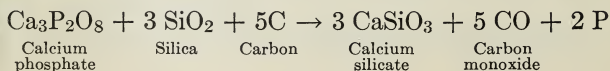
NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

475. General. Of the five elements of Group V, nitrogen is the only one that has been described. Phosphorus and arsenic, like nitrogen, are non-metals. Antimony and bismuth are metals. The *valence* of the elements of this family may be either 3 or 5 in different compounds.

PHOSPHORUS (P=31; Formula, P₄)

476. Occurrence. Phosphorus, though it does not occur native, is by far the most abundant element of the nitrogen family, making up nearly 0.1 per cent of the crust of the earth. The most important mineral containing phosphorus is *calcium phosphate*, Ca₃P₂O₈, which is found chiefly in a grayish-white amorphous form known as **phosphate rock**. Great beds of phosphate rock exist in South Carolina, Tennessee, and Florida. In these three states more than a million tons of it are obtained each year, which is used in the manufacture of fertilizers. Enormous deposits exist also in Idaho, Montana, Wyoming, and Utah. Owing to the lack of railroad facilities and to the absence of a market for fertilizers in the locality, the western phosphate beds have scarcely been touched as yet.

477. Preparation. Phosphorus is made by heating a mixture of phosphate rock with coke and sand by means of an electric arc:



The electric furnace employed is shown in Fig. 235. The arc burns between graphite electrodes which enter at the sides. The mixture of phosphate rock, coke, and sand is placed in the hopper and is fed into the furnace by a screw conveyor. The calcium silicate melts and forms a slag which is run off, while the phosphorus escapes as vapor at the bottom and is condensed under water. The crude phosphorus is purified by distillation in an iron retort, again condensed under water, and, while melted, filtered under water through chamois skin. It is then cast into sticks for sale to the manufacturer of matches.

478. White phosphorus.

The phosphorus obtained in this way is an allotropic modification known as **white phosphorus**. When freshly prepared it is a colorless, transparent, waxy solid, soft enough to cut with a knife, which melts at 44° , boils at 287° , and has specific gravity of 1.83. The specific gravity of phosphorus *vapor* referred to air is 4.31. Multiplying this by 29, we obtain 124 as the molecular weight. Hence the molecule contains *four atoms*, and the formula is P_4 .

White phosphorus is insoluble in water. It is soluble in turpentine, olive oil, and carbon disulphide, which latter liquid will dissolve 10 times its weight of white phosphorus. When this solution is poured over filter paper, the carbon disulphide evaporates and leaves finely divided phosphorus, which at once ignites spontaneously. A dilute solution of phosphorus in olive oil, when rubbed upon the face and hands, makes them

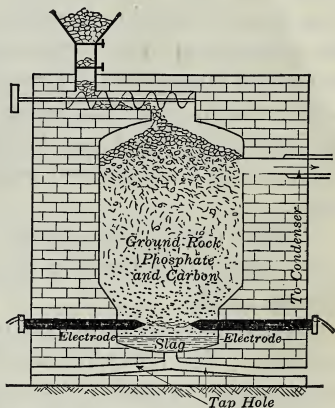


Fig. 235. Electric furnace for the manufacture of phosphorus.

luminous in the dark; it has been employed by conjurors and mediums.

White phosphorus is an *active* element. In the air it ignites at 44° and burns violently, yielding a dense white smoke of *phosphorus pentoxide*, P_2O_5 . At ordinary temperatures it oxidizes slowly, producing white fumes which smell like garlic and are luminous in the dark. As a rule the heat liberated by this slow combustion is sufficient to raise the temperature of the phosphorus to 44° , whereupon it ignites. Because of this fact white phosphorus is always handled, transported, and kept under water. It should never be touched with the fingers, for the heat of the hand may be sufficient to ignite it, and a phosphorus burn is a poisoned wound which heals with great difficulty.

White phosphorus ignites spontaneously in chlorine and burns with a pale flame to the yellow solid, phosphorus pentachloride, PCl_5 .

White phosphorus is very poisonous, and there is no reliable antidote. The effects of small quantities are cumulative, and workmen who handle it are exposed to a slow poisoning, two of the symptoms of which are a replacement of portions of the muscles of the heart by fat and a distressing decay of the bones of the jaw. It is for this reason that the use of white phosphorus in making matches has been forbidden all over the world.

479. Red phosphorus. A second allotropic form called **red phosphorus** is obtained when white phosphorus is heated to 232° in the absence of air. On a manufacturing scale, 200 lb. of white phosphorus is placed in an iron kettle, which is then sealed and heated for 10 days. The temperature must be carefully regulated, for at 260° the red phosphorus begins to change back to the white variety.

The product still contains a little white phosphorus. It is, therefore, ground under water and placed in a solution of calcium chloride of such strength that the liquid is about twice

as dense as water. The white phosphorus melts and, being lighter than the solution, rises to the top, while the red phosphorus, of which the specific gravity is 2.16, remains at the bottom.

Red phosphorus is a purplish-red powder composed of microscopic crystals. It is much denser than the white variety, is insoluble in carbon disulphide, and since it is scarcely affected by the air at ordinary temperatures, it can be transported and stored as a dry powder without danger. Red phosphorus is not luminous in the dark, and it does not ignite until heated to 240° . It has no odor. *When entirely free from white phosphorus*, it is not poisonous when swallowed. However, if red phosphorus suspended in water is injected into a vein, phosphorus poisoning results.

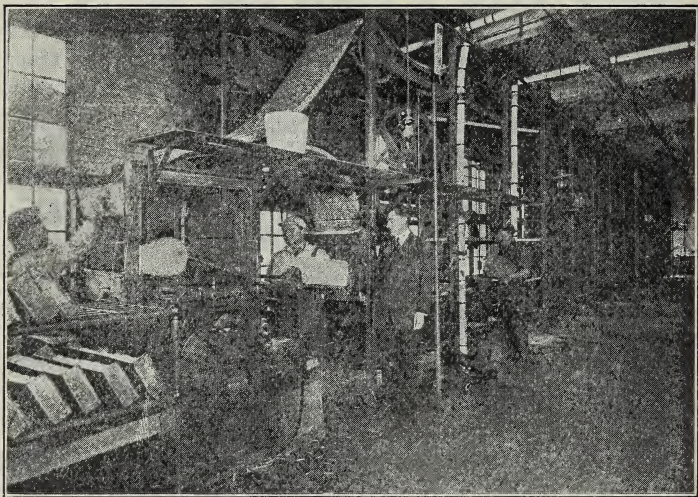
480. Uses. For the destruction of rats, mice, and roaches, poisons are obtainable that are manufactured by mixing a little white phosphorus with warm water and molasses and thickening the mass with flour. A preparation of this nature is effective, but when it is used, its highly poisonous character should never be forgotten.

The experience of the United States Navy during the World War showed that the dense cloud of phosphorus pentoxide from burning phosphorus furnished the best *smoke screen* to protect naval vessels against submarine attacks, and the element was much employed for this purpose. It was also used in hand grenades.

Phosphorus when a constituent of iron and steel injures the metal, making it brittle and worthless, but on copper its effect is the reverse. **Phosphor bronze** is a hard, tenacious alloy, almost unaffected by water. Like ordinary bronze, it is composed of copper and tin, and its superiority is due to the addition of 0.5 per cent of phosphorus.

A mixture of red phosphorus and potassium chlorate explodes with a loud report when struck with a hammer. This mixture is the basis of the paper caps used in toy pistols.

481. Matches. *Phosphorus sulphide*, P_4S_3 , is a yellow powder made by heating phosphorus with sulphur in the absence of air. A mixture of phosphorus sulphide with potassium chlorate is easily ignited by friction, and this mixture is used in the heads of matches. *Dextrin*, which is an adhesive like glue,



Courtesy of the Liberty-Rahe Match Co.

Fig. 236. Match machine carrying a million sticks through the processes of dipping and drying.

is added to prevent the head from crumbling when the match is struck.

In making matches the stick is first dipped into melted paraffin and then into a mixture of potassium nitrate, charcoal, dextrin, and enough water to form a paste. The match is then dried, which leaves it with a black head which, although very combustible, cannot be ignited by friction.

The next step is to dip the tip of the head into a paste composed of phosphorus sulphide, potassium chlorate, dextrin, and water. After being dried a second time, the match is ready for

use. When it is struck, the heat produced by friction inflames the tip, and this sets fire to the combustible material composing the bulk of the head. This in turn ignites the paraffin, and finally the wood itself is kindled.

Matches made by different companies differ somewhat in composition. Instead of potassium chlorate and potassium nitrate, other oxidizing agents, especially red lead, lead dioxide, and manganese dioxide, are used, and the pastes are often colored blue with ultramarine, red with vermilion, and other colors with various pigments.

In **safety matches** the head of the match is composed of *antimony sulphide*, Sb_2S_3 , and potassium chlorate. This mixture is not easily ignited by friction, but it takes fire at once on contact with a flame, however small. On the box is glued a mixture of red phosphorus and powdered glass. When the head of the match is drawn over this surface, a trace of the red phosphorus is torn off and burns in contact with the head, which immediately ignites and kindles the wood.

482. Phosphorus in plants and animals. All fertile soils contain phosphates, especially calcium phosphate, which are taken up by plants and converted into complex phosphorus compounds. These are found mainly in the fruit and seeds. From the plants the phosphorus finds its way into the animal tissues, where it occurs in the skeleton, in the brain, and in the nerves. The body of a full-grown man contains 600 grams of phosphorus, of which 95 per cent is in the bones and teeth as calcium phosphate, $\text{Ca}_3\text{P}_2\text{O}_8$, and the balance in the nervous system in the form of complex fats containing phosphorus. The *tartar* which collects on the teeth is chiefly composed of calcium phosphate, and the saliva contains sodium phosphate, Na_2HPO_4 . It is interesting to note that the total phosphorus of the normal human body, if liberated from the complex compounds in which it occurs, would suffice to prepare 500,000 matches or to administer a fatal dose of phosphorus to 6,000 persons.

It will be clear from these facts that phosphorus compounds are a necessity in the diet. It is calculated that the food taken each day should contain 1.5 grams of phosphorus, which of course, must be taken, not as the highly poisonous element, but in the form of compounds that can be utilized in the body. Many cases of malnutrition are due to lack of phosphorus in the diet. Among foods rich in phosphorus are milk, eggs, cheese, cereals, and nuts.

COMPOUNDS OF PHOSPHORUS

483. Phosphine, PH_3 . Phosphine corresponds to ammonia, NH_3 , but differs from it radically in properties. Phosphine is a colorless, highly combustible gas, which smells like decaying fish. It is very poisonous and has been used in gas warfare.

484. Phosphorus pentoxide, P_2O_5 . Phosphorus pentoxide is formed when either form of phosphorus is burned with abundant air supply. A small quantity can easily be prepared by burning phosphorus under a dry bell jar (Fig. 237). The phosphorus pentoxide forms snowy flakes which cling to the bell jar. By means of a funnel it can be transferred to a dry bottle, the stopper of which must be sealed with melted paraffin. The most striking thing about phosphorus

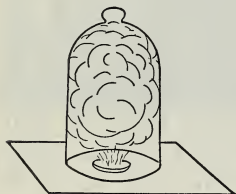
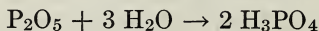


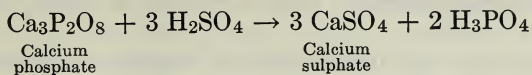
Fig. 237. Preparation of phosphorus pentoxide.

pentoxide is its attraction for water, with which it combines with a hissing noise and the evolution of much heat. The final product is *phosphoric acid*, H_3PO_4 :



485. Phosphoric acid, H_3PO_4 . Phosphoric acid forms colorless crystals which dissolve freely in water to form a sirupy,

strongly acid liquid. It is prepared commercially by decomposing phosphate rock or bone ash by means of sulphuric acid:



The calcium sulphate, which is only slightly soluble in water, is removed by filtration, and the phosphoric acid sold in the form



Courtesy of the American Agricultural Chemical Co.

Fig. 238. Hydraulic mining of pebble phosphate rock in Florida.

of a sirup which contains 50 to 85 per cent of H_3PO_4 . It is used in calico printing, in rust-proofing iron and steel, and in the preparation of beverages (“acid phosphate”).

486. “Superphosphate,” $\text{CaH}_4\text{P}_2\text{O}_8$. We have seen that calcium phosphate occurs in enormous deposits as phosphate rock. The rock is insoluble in water, and when merely powdered and used as a fertilizer, it does not give good results, because any mineral that is to be taken up by a plant must first be dissolved in the water of the soil. Hence the phosphate rock is

prepared for use by treating it with *sulphuric acid*, which converts it into *calcium hydrogen phosphate*, $\text{CaH}_4\text{P}_2\text{O}_8$, commonly called **superphosphate**. This is soluble in water and is an excellent fertilizer.

Phosphate rock occurs both in deposits of pebbles and in solid beds. Pebble deposits are usually stripped and exca-



Courtesy of the American Agricultural Chemical Co.

Fig. 239. Effect of a complete fertilizer on wheat production.

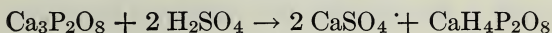
At the right an unfertilized plot yielding 5 bu. per acre; at the left a plot treated with 200 lb. of complete fertilizer per acre yielding 18 bu. per acre.

vated by *hydraulic* methods, which free the pebbles of adhering foreign matter. The beds of phosphate rock are about a foot thick and are found at a depth of about 30 ft. The overlying soil is stripped off, and the phosphate rock dug out with pick and shovel and put through a crusher. This reduces it to lumps 4 in. in diameter, which are washed in a trough by a strong current of water to remove sand and clay.

In this state the material is shipped to the manufacturer of

superphosphate, who powders it until it will pass through a sieve having 80 meshes to the inch. In a cast-iron mixer provided with a stirring device the powder is then treated with an equal weight of sulphuric acid. Acid from the lead chambers containing about one-third of its weight of water is employed, and this is the largest single use of sulphuric acid.

In 5 minutes the mixture is run into a brick-lined pit beneath the mixer called the "den," which receives successive charges until it is filled. The chemical change is as follows:



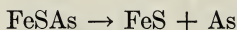
In the den the temperature rises to 100°, and as the chemical change is completed, the material stiffens into a dry, porous mass, which is dug out, pulverized, and packed into bags for sale. Usually the manufacturer mixes the superphosphate with materials containing nitrogen and potassium and markets the whole as a so-called "complete fertilizer."

Calcium hydrogen phosphate favors the growth of roots and is invaluable on root crops, especially potatoes and turnips. It hastens the ripening process and may be used to make the crop mature a week or more earlier to avoid autumnal frosts. It is an excellent application when there is reason to fear drought, as the stimulation of root growth due to the fertilizer causes the roots to penetrate deeper layers of soil and enables the plant to supply itself more liberally with moisture.

ARSENIC (As = 75; Formula, As₄)

487. Occurrence. *Native* arsenic occurs only sparingly. **Arsenopyrite**, FeSAs, is a hard, dense, silver-white mineral, which is abundant in the United States and Canada. The arsenic compounds of commerce are made from *arsenious oxide*, As₄O₆, which is obtained, chiefly in Canada, as a by-product of the smelting of ores of nickel and copper.

488. Preparation and properties. When arsenopyrite is heated, arsenic vaporizes, and iron sulphide remains:



Arsenic is made by heating arsenopyrite in a horizontal clay tube, into the mouth of which is fitted a roll of sheet iron to receive and condense the arsenic vapor.

Arsenic comes into commerce in the form of small, brittle lumps which resemble coke but are much denser. It is insoluble in water and is therefore far less poisonous than many of its compounds. When heated without access of air, it vaporizes without melting. Heated in air or in oxygen, it combines with the latter, forming *arsenious oxide*.

489. Arsenious oxide, As_2O_3 . Most nickel ores are arsenic compounds, and when they are roasted in a current of air, the arsenic combines with oxygen and collects in the flues of the furnace as arsenious oxide. The great deposits of nickel ores in the Province of Ontario, Canada, are the chief source of arsenious oxide for the United States.

Arsenious oxide is often incorrectly called *white arsenic* or simply "arsenic." It is a dense, white, crystalline powder, which vaporizes without melting when gently heated and dissolves slowly in water. It has a slightly sweetish taste and is intensely poisonous. As little as 0.06 gram has caused death. Fortunately its action on the body is slow, and there is ample time for treatment. The best antidote is freshly prepared *ferric hydroxide*, $\text{Fe}(\text{OH})_3$, which forms an insoluble compound with the arsenious oxide and renders it harmless.

In case of confusion in the household, arsenious oxide can easily be distinguished from other white powders by sprinkling a little on a red-hot coal, whereupon arsenic vaporizes, yielding a white smoke and disseminating a strong odor of garlic.

Arsenious oxide is used as a rat poison. It is employed as an addition to melted plate and window glass to oxidize impuri-

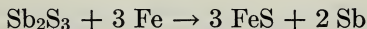
ties and improve the color and lustre of the product. The taxidermist applies it to the preservation of skins. The chief use of arsenious oxide is in the preparation of other compounds of arsenic, especially *Paris green*, *London purple*, and *lead arsenate*, which serve for protecting plants and trees against insects, moulds, and fungi.

Lead arsenate is the most important of these substances. It is the lead salt of *arsenic acid*, H_3AsO_4 , and its composition corresponds to the formula PbHAsO_4 . Lead arsenate is a white, insoluble powder, which is sold as a moist paste and which, suspended in water, is largely used as a spray by the farmer and orchardist.

Arsine, AsH_3 , corresponds to ammonia. It is a colorless, highly poisonous gas, which has been used in warfare.

ANTIMONY ($\text{Sb} = 120$)

490. Occurrence and preparation. The only important ore of antimony is **stibnite**, a lead-gray, brittle mineral which melts easily in the flame of a candle. Stibnite is *antimony sulphide*, Sb_2S_3 . To obtain antimony, crushed stibnite is melted in a crucible with iron scrap, such as the clippings from the manufacture of cans. When the mass cools, a layer of antimony is found in the bottom and one of iron sulphide above:

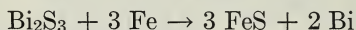


491. Properties and uses. Antimony is a silvery, brittle, crystalline metal, of specific gravity 6.7, which melts at 630° . Melted antimony oxidizes rapidly in the air, giving off a white smoke of *antimonious oxide*, Sb_4O_6 . On account of its brittleness antimony is never used alone for constructive purposes. Its most important alloys are those containing lead, with other metals. Among these are *Britannia metal*, *Babbitt metal*, *shrapnel*, and *type metal*, all of which have been discussed in

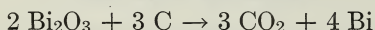
Chapter XXXV. Liquid antimony *expands* when it becomes solid, and it communicates this property to alloys containing it. Hence they form a sharp cast of the mould into which they are poured.

BISMUTH (Bi = 209)

492. Preparation. The ores of bismuth contain the native metal mixed with *bismuth sulphide*, Bi_2S_3 . In extracting the bismuth the ore is first roasted, which converts a portion of the bismuth sulphide into bismuth oxide, Bi_2O_3 . The roasted ore is then mixed with iron filings and coke and smelted in a reverberatory furnace. The iron liberates bismuth from the sulphide:



while the bismuth oxide is reduced by the carbon:



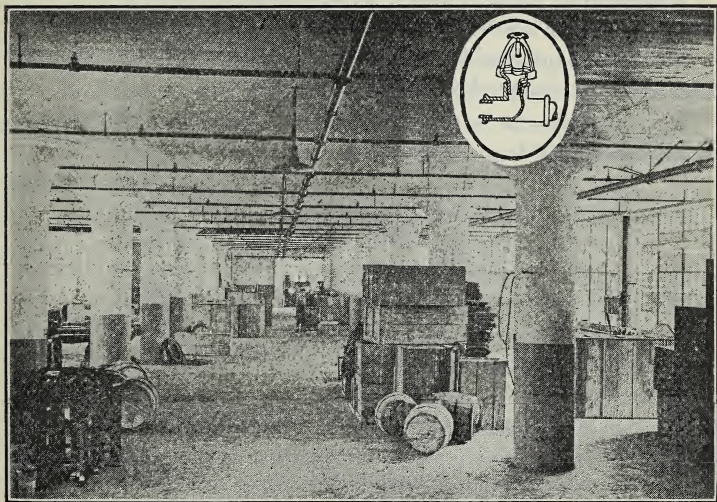
The melted bismuth collects on the hearth of the furnace.

493. Properties and uses. Bismuth is a lustrous, reddish-white, brittle metal, which melts at 270° and dissolves easily in nitric acid. Its chief use is in the preparation of alloys known as *fusible metals*, which melt at low temperatures and have important applications. Three of these alloys are given in the following table:

Alloy	Melting Point	Lead, per cent	Tin, per cent	Bismuth, per cent	Cadmium, per cent
Newton's.....	95°	32	18	50	
Rose's.....	94°	25	25	50	
Wood's.....	60°	25	12.5	50	12.5

Alloys of this nature are used in *fuses for electrical circuits*, so that if the current becomes too heavy for the wiring to carry

safely, the fuse will melt and break the circuit. In *automatic sprinklers* a perforated pipe connected with the water supply is plugged with fusible metal. In case of fire the plugs melt and release a shower which extinguishes the blaze. Boilers are often fitted with safety plugs of fusible metal, which melt if the temperature and pressure become dangerously high. Most large buildings contain fire walls, reaching from basement to



Courtesy of the Grinnell Co.

Fig. 240. Automatic sprinkler installation in a warehouse. Inset: diagram of a sprinkler head showing the fusible plug.

roof, which divide the structure into sections and localize any fire that may occur. The doors in these walls are held up by chains containing a link of fusible metal, which melts when heated and automatically allows the door to close.

494. Bismuth subnitrate, BiONO_3 . As the formula shows, bismuth subnitrate is both an oxide and a nitrate. It is made by dissolving purified bismuth in nitric acid and pouring the solution into water. It is a white, insoluble powder, which is

used as a paint and as a cosmetic and is much employed in medicine.

Bismuth oxychloride, BiOCl , is a white, insoluble powder, which is used as a cosmetic under the name "*pearl white*."

SUMMARY

Phosphorus occurs chiefly as *phosphate rock*, which is composed of **calcium phosphate**, $\text{Ca}_3\text{P}_2\text{O}_8$.

White phosphorus is made by heating phosphate rock with coke and sand in an electric furnace.

Red phosphorus is obtained by heating white phosphorus, air being excluded.

	White Phosphorus	Red Phosphorus
<i>Color</i>	Colorless	Red
<i>Odor</i>	Resembles garlic	Odorless
<i>Luminosity</i>	Luminous in the dark	Not luminous
<i>Kindling point</i>	44°	240°
<i>Behavior in air at room temperature</i>	Oxidizes and finally ignites	Unaffected
<i>Solubility</i>	Soluble in CS_2	Insoluble in CS_2
<i>Effect on body</i>	Poisonous	Non-poisonous
<i>Combustion product</i>	P_2O_5	P_2O_5

Calcium hydrogen phosphate ("**superphosphate**") is made by treating phosphate rock with sulphuric acid.

The **arsenic** of commerce resembles crushed coke but is denser.

Arsenious oxide, As_4O_6 , is a dense, white powder, which is often called **white arsenic**. It is a powerful poison.

Lead arsenate, PbHAsO_4 , is a white insoluble powder, which is largely used as an insecticide and fungicide spray.

Antimony is a silver-white, brittle, crystalline metal, used as a hardening constituent in alloys containing lead and other metals.

Bismuth is a reddish-white, brittle metal which finds application in fusible alloys and in making the important medicine bismuth subnitrate, BiONO_3 .

EXERCISES

1. Make, in parallel columns, a comparison of white and red phosphorus. Which is the more active? Why?

2. What is the daily phosphorus requirement of the body? How can it be supplied?

3. Free white phosphorus is poisonous, and yet phosphorus is a necessity in the diet. Explain.

4. Enumerate the metallic and the non-metallic characteristics of arsenic, antimony, and bismuth. Have nitrogen and phosphorus any metallic properties? Do the metallic properties increase or decrease with increasing atomic weight from nitrogen ($N=14$) to bismuth ($Bi=208$)?

5. How are fusible alloys made? Mention three of their applications.

6. Commercial bismuth, intended for making fusible alloys, may contain lead, arsenic, antimony, copper, and other metallic impurities. Could this grade of bismuth be used for preparing bismuth subnitrate?

7. Lead arsenate is now by far the most important compound of arsenic. Explain.

8. Why are safety matches so called?

9. How could you transform white phosphorus to red? Red to white? Would it be necessary to exclude air from the apparatus? Why?

10. A liter of the vapor of phosphorus weighs about 62 times as much as a liter of hydrogen at the same temperature and pressure. How many atoms are there in the phosphorus molecule? Why? Solve by inspection.

11. Solid type metal *floats* on liquid type metal. What does this indicate? To which metal of the alloy is this behavior due? Give two reasons for the use of this metal in the alloy.

12. Give reasons for the belief that red and white phosphorus are two forms of the same element.

13. 30 kg. of impure phosphate rock containing 58 per cent of $\text{Ca}_3\text{P}_2\text{O}_8$ are heated in an electric furnace with coke and sand. How many kilograms of phosphorus are obtained?

14. 50 kg. of antimony ore containing 60 per cent of Sb_2S_3 are melted with iron. How many kilograms of antimony are obtained?

15. How many liters of oxygen are needed to convert 93 grams of phosphorus into P_2O_5 ? Take the weight of 1 liter of oxygen as 1.43 grams.

16. How many liters of air are needed to burn 123 grams of phosphorus to P_2O_5 ? Assume that air contains 21 per cent by volume of oxygen.

REVIEW QUESTIONS

1. Mention, in addition to phosphorus, four other elements that exist in different allotropic forms. Give reasons in each case for the belief that the different forms are really composed of the same element.

2. What three elements are most important in commercial fertilizers?

3. What is Avogadro's Hypothesis? In what way does it enable us to ascertain the number of atoms in the molecule of a gaseous element?

4. Compare sodium with white phosphorus both physically and chemically. Why is sodium kept under kerosene, and white phosphorus under water?

5. What is *Babbitt metal*? *Type metal*? *Pewter*? *Britannia metal*? *Hard lead*? *Shrapnel alloy*? What alloy is used for making shot?

CHAPTER XXXVII

GROUPS VIA AND VIIA. THE CHROMIUM FAMILY; MANGANESE

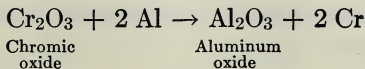
CHROMIUM, TUNGSTEN, URANIUM; MANGANESE

495. General. Chromium, tungsten, and uranium belong in the sixth group of the periodic system, along with the Sulphur Family, while manganese is a member of Group VII. All four elements are metals which are found only in their compounds. Manganese is the most abundant. Chromium, tungsten, and manganese have important practical applications.

CHROMIUM (Cr = 52)

496. Occurrence. The most abundant mineral containing chromium is **chromite**, or **chrome iron ore**, which is a double oxide of iron and chromium, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The formula is often written FeCr_2O_4 . Chromite is a hard, iron-black substance, which melts only at a very high temperature and so is used as a lining for the hearths of steel furnaces. It is mined in New Caledonia, New South Wales, Asia Minor, and the United States.

497. Preparation. Pure chromium is made commercially by placing in a crucible a mixture of chromic oxide, Cr_2O_3 , with one-third of its weight of granulated aluminum and igniting the mixture with a special fuse. The chromic oxide is reduced by the aluminum:



The chemical change spreads through the mass, which is carried to a temperature of $3,000^{\circ}$ by the large amount of heat liberated. On cooling, the bottom of the crucible is found to be occupied by a dense layer of metallic chromium, which is covered by a slag of aluminum oxide.

498. Properties. Chromium is a hard, brittle, silvery metal, which retains its lustre in the air. It is slightly less dense than iron and melts at a somewhat lower temperature. When intensely heated, it burns to chromic oxide, producing brilliant sparks. It dissolves in hydrochloric acid but is unaffected by nitric acid.

499. Uses. Chromium imparts great hardness to steel and is largely used in the production of special steels which are called "chrome steels." Steel for burglar-proof safes and vaults contains 2 per cent of chromium; balls and rollers for bearings contain 1 per cent or more, and armor plate 1.5 per cent. Chrome steel is also used for armor-piercing projectiles and for automobile gears. Table knives made of steel containing 13 per cent of chromium are on the market under the name "stainless cutlery." They are as hard as the best steel, and their silvery lustre is unaffected by the acids found in food.

500. Ferro-chrome. Chrome steels are sometimes made by introducing into melted steel metallic chromium made by the process just described. As a rule, however, it is cheaper to use instead of metallic chromium a commercial product called **ferro-chrome**, which contains about two-thirds of its weight of chromium, the balance being chiefly iron and carbon. Ferro-chrome is made by smelting chromite with iron and coke in an electric furnace at a high temperature.

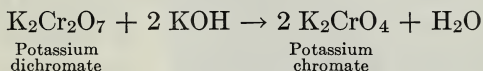
COMPOUNDS OF CHROMIUM

Chromic oxide, Cr_2O_3 , is a green powder which is used under the name "**chrome green**" for painting on china and for coloring bank notes.

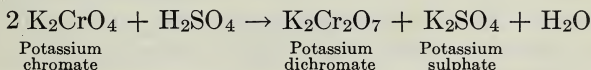
501. Potassium dichromate, $K_2Cr_2O_7$. Potassium dichromate is made by heating chrome iron ore with potassium carbonate in a reverberatory furnace. Lime is added also to keep the mixture from melting, for oxygen is absorbed in the chemical change, and this would occur only very slowly if the mass became completely liquid and lost all its porosity.

Potassium dichromate forms orange-red, anhydrous crystals, which are only sparingly soluble in cold water but dissolve freely when the liquid is heated. It is employed in lithography and as a mordant in dyeing wool. Its largest use is in tanning *chrome* leather for the uppers of shoes.

Potassium chromate, K_2CrO_4 , is formed when a solution of potassium hydroxide or of potassium carbonate is added to a solution of potassium dichromate:

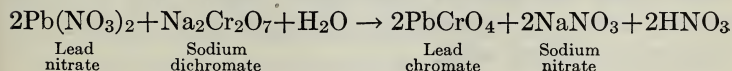


Potassium chromate is bright lemon-yellow and is freely soluble in water. When an acid is added to its solution, the yellow color changes to red, and potassium dichromate is formed:



Sodium dichromate, $Na_2Cr_2O_7$, is made by heating chrome iron ore with sodium carbonate and lime. It forms red crystals of the formula $Na_2Cr_2O_7 \cdot 2 H_2O$, which are quite soluble in water. It is cheaper than potassium dichromate and is rapidly displacing the latter in dyeing and tanning.

502. Lead chromate, $PbCrO_4$. Lead chromate is made by mixing a solution of lead nitrate with one of sodium dichromate:



Lead chromate is a brilliant yellow powder, which is insoluble in water. It is known commercially as "**chrome yellow**" and is a very important yellow pigment.

Zinc chromate, ZnCrO_4 , and **barium chromate**, BaCrO_4 , resemble chrome yellow and, like it, are extensively used as yellow pigments. All three have a remarkable tendency to prevent the rusting of iron. Ground with linseed oil with very little thinner and drier, they are extensively used as a protective coat for structural steel. Zinc chromate is perhaps the best paint known for this important purpose.

All chromates and dichromates are *poisonous* and handling them is an unwholesome occupation. Malignant ulcers are frequent among the workmen and perforation of the septum between the nostrils almost universal. Workmen who deal with lead chromate are liable also to the danger of lead poisoning. Chromates should not be used for coloring paper intended for wrapping food products.

TUNGSTEN ($W=184$)

503. Tungsten is a gray lustrous metal which has the very high specific gravity of 19.5 and the enormously high melting point of $3,350^\circ$. It is intensely hard, quite unaffected by air, water, and the ordinary acids, and is malleable and ductile at high temperatures.

The properties of tungsten make it a very suitable material for the construction of government standards of weight and length, and it has been proposed to make standard meters and kilograms of tungsten as a substitute for the expensive alloy of platinum and iridium now employed for this purpose. It has found wide application as a cheap and excellent substitute for platinum in electrical contacts in switches and vibrators, in spark plugs for internal combustion engines and in X-ray tubes. Alloys of tungsten are employed as a substitute for platinum in dental work.

Tungsten is a good conductor of the electric current, and its melting point is far higher than that of any other metal. These properties make it the best possible material for the filaments of incandescent electric lamps, and over a million feet of fine tungsten wire is used daily for this purpose. Tungsten phonograph needles have been on sale since 1915; because of the great hardness of the metal, a single needle can be used many times before replacement is necessary.

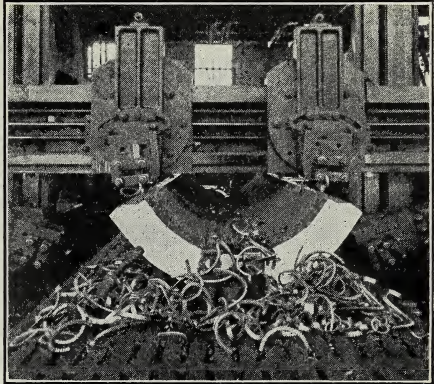
Over 90 per cent of the total output of tungsten goes into the steel industry, where it is consumed in the manufacture of special steels that are called **high-speed tool steels**.

These steels are used for making cutting tools for working steel and other metals on the lathe. A typical steel for this purpose has the following composition:

	Per cent
Tungsten.....	18
Chromium.....	4.5
Vanadium.....	0.6
Carbon.....	1

the balance being chiefly iron.

A tool made of this steel can be used in metal cutting when the lathe is run at such a high speed that the tool becomes red-hot. Even under these conditions the tungsten-steel tool retains its hardness and its cutting edge. A tool made of ordi-



Courtesy of the Bethlehem Steel Co.

Fig. 241. Tungsten-steel tools taking cuts $1\frac{1}{2}$ in. wide and $\frac{1}{8}$ in. deep in nickel-chrome steel armor plate at a speed of 18 ft. per minute.

nary steel would at once be softened and spoiled by this treatment.

Steel containing 6 per cent of tungsten retains magnetism remarkably well and is much used in electrical measuring instruments.

URANIUM ($U = 238.2$)

504. Uranium is a grayish-white, malleable metal resembling nickel in appearance but differing greatly in density, for the specific gravity of uranium is 18.7, and it is, therefore, more than twice as dense as nickel (sp. gr. 8.9).

A special interest attaches to uranium because it possesses the highest atomic weight of all of the elements. Connected

with this is the fact that uranium was the first element in which the wonderful attribute of **radioactivity** was discovered. Uranium and all of its compounds continually give off *rays* which act upon the photographic plate, cause air to become a conductor of electricity, and have many other remarkable properties.

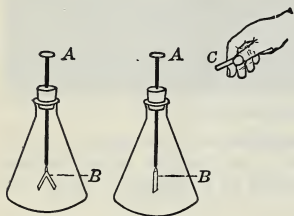


Fig. 242. A charged electroscope discharged by uranium.

The effect of uranium and other radioactive elements upon air is shown in Figure 242. The sketch at the left is a simple electroscope in which two strips of gold leaf, *B*, supported on a wire, have been charged with electricity through the knob *A*. They diverge because the repulsion of the charges drives them apart. But when a piece of uranium *C* is brought near the wire, as in the sketch at the right; the air becomes a conductor and the charge is lost, so that the two strips of gold leaf fall together.

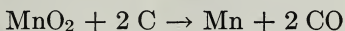
Compounds of uranium are added in the melting pot to glass intended for the lenses of the lamps of automobiles. The

presence of the uranium makes the glass yellow and fluorescent and cuts off the glare which is so blinding to other motorists and to pedestrians.

MANGANESE (Mn = 55)

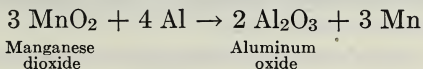
505. Occurrence. The chief ore of manganese is **pyrolusite**, a black, crystalline mineral soft enough to soil the fingers, which is mined in Brazil, India, Russia, and the United States. Pyrolusite is *manganese dioxide*, and its composition is indicated by the formula MnO_2 .

506. Preparation and properties. Manganese dioxide can be reduced by mixing it with coke or charcoal and heating in an electric furnace:



but the manganese will take up carbon and become impure.

Pure manganese is easily obtained by the **thermit process**. A mixture of manganese dioxide and granulated aluminum is ignited in a refractory crucible by a fuse:

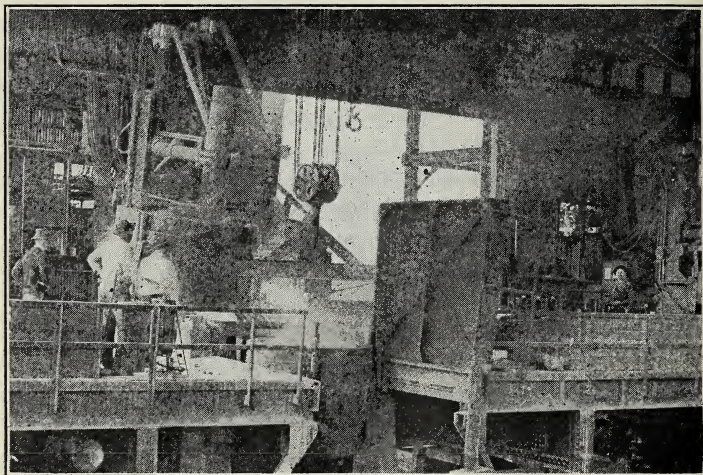


The heat liberated carries the mass to a temperature of $3,000^\circ$. On cooling, the manganese is found in the bottom of the crucible and above it a slag composed of aluminum oxide.

Manganese is a brittle, gray metal the lustre of which is tinged with red. Its specific gravity (7.4) is less than that of iron, and it melts more readily. In other respects it resembles iron both in physical properties and in chemical conduct. Manganese rusts in moist air, liberates hydrogen slowly from water when heated, and dissolves easily in acids.

507. Alloys of manganese. **Spiegeleisen** or **specular pig iron** is an alloy containing 15–20 per cent of manganese, the balance

being chiefly iron and carbon. It is made by smelting mixtures of manganese ores and iron ores with coke and limestone in a blast furnace. **Ferro-manganese** is a more expensive alloy, similar to spiegeleisen, but containing up to 70 per cent of manganese. Both alloys are used in enormous quantities in



Courtesy of the Southern Manganese Corporation.

Fig. 243. Manufacture of ferro-manganese in the electric furnace.

the steel industry, and we shall meet them again when we study that subject.

Manganese steel contains 14 per cent of manganese, the balance being mainly iron with a little carbon. It is so hard and tough that it is impossible to drill it or work it on a lathe. It is used for the jaws of rock-crushers, for screens for sorting the different sizes of coke, for the "frogs" of railroad switches, and in general where extreme hardness and tenacity are desirable.

Manganese bronze is an alloy of copper, tin, and manganese. It is almost as tenacious as iron, and it has the great merit of

being unaffected by water and air. It is largely employed for the propellers of steamships.

508. Manganese dioxide, MnO_2 . Manganese dioxide can be made artificially, but for practical purposes it is cheaper to powder a pure grade of pyrolusite. Manganese dioxide is essential as a **depolarizer** in dry cells. When added to melted glass, it removes the green tint due to iron compounds, and it is largely used for this purpose. We have noted the use of manganese dioxide for generating chlorine with hydrochloric acid in the laboratory and its employment as a catalyst in preparing oxygen from potassium chlorate. The most important use of native manganese dioxide is in the manufacture of spiegeleisen and ferro-manganese.

509. Potassium permanganate, KMnO_4 . The indispensable salt *potassium permanganate* is made by melting manganese dioxide with potassium hydroxide and potassium chlorate at a low red heat. The fused mass is dissolved in water, and a current of carbon dioxide is passed through the solution until its color changes from green to a deep purple. The liquid is then evaporated and cooled to allow the potassium permanganate to crystallize.

Potassium permanganate forms dark, rhombic crystals with a greenish lustre. It is soluble in water, and the solution has a magnificent purple color. The oxygen of potassium permanganate is only loosely held, and its solution is, therefore, a strong *oxidizing agent*. It is constantly employed for this purpose in the laboratory. The oxidation can be controlled by adding the potassium-permanganate solution little by little to the solution to be oxidized so long as the purple color disappears. When the purple color remains permanent, showing that potassium permanganate is no longer being consumed, the oxidation is finished.

Potassium permanganate is an excellent disinfectant, and its solution is employed for this purpose under the name "**Condy's fluid**." It is also used in bleaching, in dyeing, for

producing a brown coloration on wood, as a gargle for inflammation of the throat, and as a specific against certain diseases of poultry.

SUMMARY

The most important mineral containing **chromium** is *chromite* or *chrome iron ore*, FeCr_2O_4 .

Chromium is made by reducing chromic oxide, Cr_2O_3 , (a) by *carbon* in an electric furnace, (b) by *aluminum* according to the thermit process.

Ferro-chrome is an alloy of chromium, iron, and carbon. It is used in making chrome steel, which is very hard and tenacious.

The most important **compounds of chromium** are the following:

Potassium dichromate.....	$\text{K}_2\text{Cr}_2\text{O}_7$
Sodium dichromate.....	$\text{Na}_2\text{Cr}_2\text{O}_7$
Lead chromate.....	PbCrO_4
Zinc chromate.....	ZnCrO_4
Barium chromate.....	BaCrO_4

Tungsten is the metal which forms the filament of the "Mazda" lamp. Its chief use is in making high-speed tool steels.

Uranium has the highest atomic weight of all of the elements. Uranium and all of its compounds are **radioactive**.

Manganese is obtained from manganese dioxide MnO_2 , which is found in nature as the mineral *pyrolusite*.

Spiegeleisen and **ferro-manganese** are alloys of manganese with iron and carbon which are used in enormous quantities in the steel industry.

The addition of a high percentage of manganese imparts extreme hardness and tenacity to steel.

Potassium permanganate, KMnO_4 , forms dark crystals which dissolve in water with an intense purple color.

EXERCISES

1. Compare chromium and manganese in their effects upon the properties of steel.
2. The name "chromium" is derived from a Greek word meaning *color*. Why was this name given to a *white* metal?
3. How could you make zinc chromate?
4. Refer to an atlas and give the location of New Caledonia.
5. Using parallel columns, make a comparison between *manganese* and *magnesium*. Include occurrence, preparation, properties, and uses.
6. How could you obtain manganese from pyrolusite? What use could be made of the other product of the process?
7. All permanganates when dissolved in water have the same beautiful purple color. Why?
8. What properties of tungsten fit it especially to serve as the filament of incandescent electric lamps?
9. In attempting to decolorize glass, what would be the effect of adding too much manganese dioxide.
10. Like antimony, manganese is used only in alloys, never alone. Why?
11. Manganese dioxide is sometimes adulterated with coal dust. What would be the result of using such impure manganese dioxide to catalyze the production of oxygen from potassium chlorate?
12. Calculate the percentage composition of (a) *chromite*, FeCr_2O_4 , (b) *chromic oxide*, Cr_2O_3 .
13. How many grams of chromium can be made by reducing 1,630 grams of chromic oxide by the thermit process?
14. How many tons of potassium dichromate could be made from 100 tons of pure chromite if there were no loss in the *process*?
15. Calculate the percentage composition of manganese dioxide.
16. How many grams of oxygen are there in a kilogram of potassium permanganate?

CHAPTER XXXVIII

GROUP VIIB. THE CHLORINE FAMILY OR HALOGENS

FLUORINE, CHLORINE, BROMINE, IODINE

510. General. The Chlorine Family of elements, often called the **halogen**, or "salt-forming," group, is an excellent example of a natural family of elements. The regular variation in physical properties with increasing atomic weight is shown in the following table:

	Fluorine	Chlorine	Bromine	Iodine
SYMBOL.....	F	Cl	Br	I
FORMULA.....	F ₂	Cl ₂	Br ₂	I ₂
ATOMIC WEIGHT.	19	35.5	80	127
COLOR.....	Pale yellow	Greenish yellow	Red	Gray-black
STATE.....	Gas	Gas	Liquid	Solid
MELTING POINT.	-223°	-102°	-7°	113°
BOILING POINT..	-187°	-34°	63°	184.4°
VALENCE.....	1	1	1	1

From this table it is evident that as the atomic weight increases from 19 to 127, the intensity of the color grows from pale yellow to black, and the physical state at ordinary temperatures changes from that of a gas to that of a solid.

The halogen elements are usually *univalent*. They are very *active* non-metals and are, therefore, found in nature only in their compounds. Chlorine, which has already been studied, is the most abundant.

FLUORINE (F=19; Formula, F₂)

511. Occurrence. The most important mineral containing fluorine is **fluorite**, commonly called **fluor spar**, which is *calcium fluoride*, CaF₂ (§ 388). Fluorite is often found with ores of lead and zinc. It forms beautiful transparent cubical crystals, which frequently have a violet-blue color but may be yellow, green, or colorless. Fluorite melts readily and is used as a *flux*, or slag-forming agent, in metallurgical work. It is also employed in making opal glass and in the preparation of hydrofluoric acid.

Cryolite, Na₃AlF₆, is a white mineral with a greasy lustre found in Greenland. It is employed in the preparation of aluminum, alum, and washing soda and in making opal glass.

512. Preparation.

Fluorine was first made by *Moissan*, in 1886, by the electrolysis of liquid anhydrous hydrogen fluoride, HF, in the apparatus of Figure 244. Anhydrous hydrogen fluoride is a non-conductor, and

therefore a little potassium hydrogen fluoride is dissolved in it to make it conduct the electric current. This solution is placed in the platinum U-tube at the right of the diagram and is surrounded by a freezing mixture. The hydrogen set free at the cathode is allowed to escape, while the fluorine formed at the anode is freed from hydrogen fluoride by condensation and by passing it over sodium fluoride and collected for experimental purposes in dry test tubes.

513. Properties. Fluorine is a gas with a color similar to that of chlorine but paler. Its odor resembles that of chlorine,

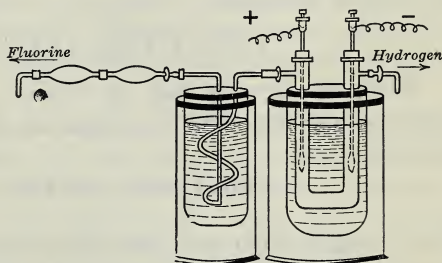
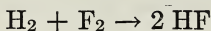


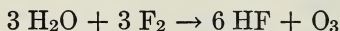
Fig. 244. Apparatus for the isolation of fluorine.

but fluorine is even more irritating and poisonous than chlorine. Liquid fluorine is yellow and has the same specific gravity as water.

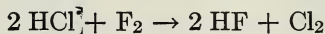
Fluorine is a typical non-metal and is the most active of the elements. It combines directly with combustion with most of the other elements and acts violently on many compounds. Its affinity for hydrogen is especially strong. A mixture of hydrogen and fluorine explodes at once, even in the dark, hydrogen fluoride being formed:



Fluorine also withdraws hydrogen from all compounds containing that element. Water is explosively decomposed by it, hydrogen fluoride being formed and oxygen liberated, chiefly in the form of ozone:

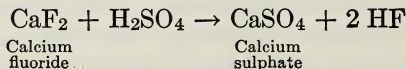


When mixed with half its volume of fluorine, hydrogen chloride explodes, with formation of hydrogen fluoride and chloride:



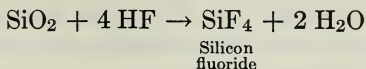
Wood contains hydrogen, and when liquid fluorine is spilled on the floor, a flame flashes up which is due to the instant combination of the fluorine with the hydrogen of the wood.

514. Hydrogen fluoride, HF. Hydrogen fluoride is made by heating a mixture of powdered calcium fluoride and concentrated sulphuric acid in a lead retort:



Hydrogen fluoride is a colorless, poisonous gas. It is easily condensed by cold, forming a colorless liquid which boils at 19°. Hydrogen fluoride is freely soluble in water, yielding a strongly acid liquid called **hydrofluoric acid**.

The most remarkable property of hydrofluoric acid is its action upon *silica*, SiO_2 , which is at once dissolved by it:



Since glass is rich in silica, hydrofluoric acid attacks it, dissolving the silica and converting the calcium and sodium into fluorides. For this reason glass bottles cannot be employed as containers for hydrofluoric acid. It is kept in bottles of hard paraffin, upon which it has no action.

The effect of hydrofluoric acid upon the body is to produce poisoned sores which heal with great difficulty. It is much more dangerous than the ordinary acids, and in working with it in the laboratory great care must be taken not to get it on the flesh. In the industries workmen who use it suffer from respiratory irritation, inflammation of the eyes, and obstinate ulcers on the skin.

The chief use of hydrofluoric acid is in *etching glass*. The method can be illustrated by covering a warm glass plate with a thin layer of melted paraffin, allowing the plate to cool until the coating becomes solid, and writing a word upon the plate with a pin, taking care to penetrate to the glass. Hydrofluoric acid is now applied by means of a brush. After a time the paraffin can be removed by dipping the plate into warm water, and the word will be found permanently etched into the glass.

In industrial work the pattern is printed on paper in an acid-proof varnish made of asphalt, wax, and oil of turpentine, and the printed surface pressed tightly against the glass. The paper is then cautiously withdrawn, leaving the pattern upon the glass, the portions to be etched remaining bare. Brushing over with hydrofluoric acid yields a clear, transparent etching; if a dull-white appearance is desired, a mixture of calcium fluoride and sulphuric acid is employed.

BROMINE (Br = 80; Formula, Br₂)

515. Occurrence and extraction. Bromine occurs chiefly in solution as *bromine ions*, Br⁻. Sea water contains them, and it was in sea water that bromine was discovered by the French chemist *Balard*, in 1826.

Small percentages of bromine ions are contained in the waters of salt springs in Michigan and Ohio. When such a water is electrolyzed, bromine *molecules*, Br₂, are liberated at

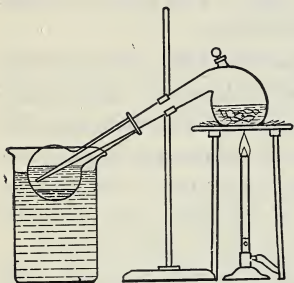
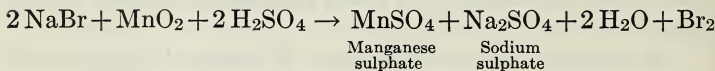


Fig. 245. Laboratory preparation of bromine.

the negative pole and at once dissolve in the liquid with a red color. The solution is then transferred to another vessel and distilled at a gentle heat. Bromine boils at 63° and, therefore, vaporizes before the water. It is condensed by cooling in a separate receiver. In a similar way bromine is obtained at Stassfurt, Germany, where it occurs as an impurity in the deposits of potassium salts.

516. Laboratory preparation. In the laboratory, bromine can be obtained by distilling sodium bromide or potassium bromide with manganese dioxide and sulphuric acid (Fig. 245):



Distillation with manganese dioxide and sulphuric acid is also employed on a large scale in obtaining bromine from the waters of salt springs.

517. Properties. Just as mercury is the only liquid metal, so bromine is the only liquid non-metallic element. It is a deep-red, opaque liquid with a specific gravity of 3.2, which gives

off a red suffocating vapor as soon as the bottle containing it is opened. It boils at 63° and freezes at -7° to a greenish-black solid.

Liquid bromine is caustic to the flesh. Its vapor has a most offensive odor and attacks the membranes of the eyes, nose, and throat even more violently than does chlorine. Bromine dissolves in 100 times its weight of water, forming a red solution called **bromine water**, which is employed in the laboratory as a powerful oxidizing agent.

518. Chemical conduct. Bromine is an active element, though less so than fluorine or chlorine. Thus, a mixture of hydrogen with bromine vapor does not explode, even under the influence of electric sparks, but when the mixture is passed through a red-hot tube, union takes place, and *hydrogen bromide*, HBr , is formed. Bromine converts the metals into their bromides, often with combustion. Thus, tin and antimony ignite when dropped into bromine, and potassium explodes with a loud report. Phosphorus also detonates on contact with bromine.

519. Uses. The chief use of bromine is in the photographic industry, large quantities of it being consumed in the manufacture of photographic films, plates, and paper. We have seen that in all three products the sensitive layer consists essentially of *silver bromide*, AgBr . Bromine is also used in making dyestuffs. Another important use of bromine is in the preparation of *potassium bromide* and *sodium bromide*, both of which are much employed in medicine.

Railroads and other transportation companies regard bromine as dangerous freight and object to receiving it. It is usually shipped, therefore, in the form of potassium bromide or of iron bromide.

520. Compounds of bromine. The bromine compounds resemble closely the corresponding compounds of chlorine. **Hydrogen bromide**, HBr , like hydrogen chloride, HCl , is a colorless, suffocating gas, excessively soluble in water to a

strongly acid liquid which is called **hydrobromic acid**. **Sodium bromide**, NaBr, and **potassium bromide**, KBr, have been mentioned under the corresponding metals. Like sodium chloride, they crystallize in cubes and resemble it in appearance, taste, and solubility. Sodium bromide can be made more cheaply than potassium bromide, but it does not crystallize as well and is more difficult to purify. For these reasons it does not displace potassium bromide, which, both in medicine and photography, is the most important bromine compound.

521. Tests for bromine. In testing a solution for bromides chlorine water is added to liberate the bromine, and the liquid is then shaken with a little chloroform, which extracts the bromine from the solution. A deep-red layer composed of a solution of *bromine in chloroform* collects at the bottom of the test tube under the aqueous liquid.

IODINE (I=127; Formula, I₂)

522. Occurrence and extraction. Sea water contains 2 parts per million by weight of iodine. This is taken up by seaweeds, and when they are dried and burned, **sodium iodide**, NaI, remains in the ashes. It was in the ashes of seaweed that iodine was discovered by *Courtois*, a Parisian saltpeter maker, in 1811.

For many years the iodine of the world was obtained solely from seaweed, but a cheaper supply has been found in the *sodium-nitrate* deposits of Chile, which contain 0.1 per cent of iodine. Most of the iodine of the world is now obtained from this source, and the supply exceeds the demand, so that new uses are needed to absorb the output.

523. Laboratory preparation. In the laboratory, iodine can be obtained like bromine, by distilling sodium iodide or potassium iodide with manganese dioxide and sulphuric acid:

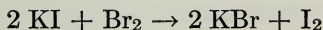
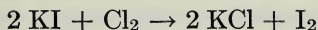


The apparatus is similar to that shown in Figure 245. The liberated iodine forms a magnificent purple vapor, which fills the retort and condenses in the cooled receiver to grayish-black crystals. Iodine is obtained from the ashes of seaweed by the same process.

524. Physical properties. Iodine forms lustrous, grayish-black crystals nearly 5 times as dense as water, which vaporize slowly at ordinary temperatures and have an odor like that of chlorine but far less irritating. It melts at 113° and boils at 184° , passing into a beautiful purple vapor which when cooled condenses directly to the solid state.

Iodine is very slightly soluble in water, but it dissolves freely in a water solution of potassium iodide, in alcohol, ether, carbon disulphide, and chloroform. The first three solutions have the brown color which is familiar in the druggist's "*tincture of iodine*"; the last two are deep purple, like iodine vapor.

525. Chemical conduct. Iodine, though an energetic non-metal, is less active than the other three elements of the Chlorine Family. Its tendency to unite with hydrogen is feeble, for a mixture of hydrogen and iodine vapor combines only partially when gently heated, and the hydrogen iodide formed is again broken up if the temperature is raised to a red heat. The inferior activity of iodine is also shown by the fact that both chlorine and bromine liberate iodine from its compounds with the metals:



Iodine combines with most of the metals at a gentle heat. In the case of mercury, grinding in a mortar with iodine in the cold is sufficient to bring about chemical union. Like the other elements of the group, iodine is *univalent* toward hydrogen and the metals.

526. Uses. Iodine is used in the manufacture of dyestuffs and medicinal chemicals. The druggist's **tincture of iodine** is an alcoholic solution containing $2\frac{1}{2}$ per cent of iodine. His **liquor iodi fortis** consists of alcohol in which 12 per cent of iodine has been dissolved. Both are poisonous and are only for external use, being usually painted on the skin, which they color deep brown. They are used as remedies for sore throat and sprains and for disinfecting the surface of the body before surgical operations. The manufacture of the important surgical antiseptic **iodoform**, CHI_3 , and of **potassium iodide**, KI , consumes a large part of the output of iodine.

527. Compounds of iodine. **Hydrogen iodide**, HI , resembles hydrogen chloride. It is a colorless, suffocating gas, which is excessively soluble in water. The solution is an active acid which is known as **hydriodic acid**.

Silver iodide, AgI , is a yellow insoluble powder. Along with silver bromide it is contained in the sensitive layer of photographic plates and films.

Potassium iodide, KI , is by far the most important compound of iodine. It forms colorless cubical crystals which are freely soluble in water and in alcohol. It is much employed in medicine and is also used in photography.

528. Test for iodine. A solution suspected to contain an iodide is mixed with chlorine water to liberate the iodine. Dilute starch paste, freshly prepared by boiling a little starch with water and cooling, is then added. If iodine is present, a deep blue color is produced. The test is both delicate and characteristic. Conversely, a solution containing free iodine serves as a *test for starch*, in food products, for instance.

SUMMARY

The most important minerals containing **fluorine** are *fluorite*, CaF_2 , and *cryolite*, Na_3AlF_6 .

Fluorine is obtained by the electrolysis of anhydrous hydrogen fluoride, HF .

Hydrogen fluoride is a colorless, caustic, poisonous gas. Its solution in water is **hydrofluoric acid**, which is used in etching glass.

Bromine is contained in sea water, in the waters of salt springs, and in the salt deposits of Stassfurt. It is a dense liquid which gives off a red, suffocating vapor.

Hydrogen bromide, HBr , resembles hydrogen chloride.

Potassium bromide, KB , is largely used in medicine and photography.

Iodine is obtained from the sodium-nitrate deposits of Chile. It forms plates which have somewhat the color and lustre of graphite.

Hydrogen iodide, HI , resembles hydrogen chloride.

Potassium iodide, KI , is the most important iodine compound.

EXERCISES

1. How could you ascertain whether a given substance was a chloride, a bromide, or an iodide?
2. A student analyzing a clear aqueous solution supplied to him finds it to contain a silver compound. Is it desirable to test the liquid for chlorides, bromides, and iodides? Why?
3. An aqueous solution of hydrogen fluoride is an electrolyte, but liquid anhydrous hydrogen fluoride is a non-conductor. Why?
4. Devise two methods of separating a mixture of powdered iodine with finely divided graphite.
5. Enumerate the properties that are common to the four halogen elements.
6. Which oxide of nitrogen resembles bromine vapor in appearance? How could you distinguish the two?
7. How would you test a potato for starch?
8. Bromine, though a good disinfectant and bleaching agent, is never employed for these purposes. Why not?
9. How could you make potassium bromide from hydrobromic acid?

10. Compare the Chlorine Family with the Sodium Family.
11. How many liters of gaseous hydrogen fluoride can be made by heating 20 grams of fluorite with sulphuric acid?
12. How many grams of calcium sulphate and how many grams of hydrogen fluoride are formed when 50 grams of calcium fluoride are heated with sulphuric acid?
13. How many grams of bromine can be obtained by passing chlorine into 6 kg. of a solution containing 0.25 per cent by weight of magnesium bromide, MgBr_2 ? How many liters of chlorine are needed? ($\text{MgBr}_2 + \text{Cl}_2 \rightarrow \text{MgCl}_2 + \text{Br}_2$)
14. How many grams of iodine can be obtained by leading chlorine into 1 kg. of a solution containing 1 per cent by weight of potassium iodide? How many cubic centimeters of chlorine are needed?
15. How many grams of iodine can be obtained by heating 43.5 grams of manganese dioxide with the proper quantities of potassium iodide and sulphuric acid?
16. How many grams of manganese dioxide are needed to liberate 63.5 grams of iodine with the needful amounts of potassium iodide and sulphuric acid?

CHAPTER XXXIX

GROUP VIII. THE IRON FAMILY AND THE PLATINUM FAMILY

IRON, NICKEL, COBALT; PLATINUM

529. General. The Eighth Group of the periodic system is composed solely of metals, of which it includes two families, the Iron Family, including *iron*, *cobalt*, and *nickel*, and the Platinum Family, which comprises six metals of which *platinum* is the most familiar.

530. The Iron Family. Iron, nickel, and cobalt are magnetic, grayish-white, *base* metals, which have a specific gravity in the neighborhood of 8 and melt at a white heat. They oxidize when heated in the air and are attacked by the ordinary acids. They occur native only in small quantities and are obtained entirely from their compounds.

IRON (Fe = 56)

531. Occurrence. *Native* iron occurs chiefly in meteorites, many of which consist of iron alloyed with nickel, cobalt, and other metals. The vapor of iron is one of the chief constituents of the sun, and compounds of iron occur so freely in the earth's crust that the metal stands fourth among the elements in point of abundance, making up 4.44 per cent of the accessible portion of our planet.

Compounds of iron are the great coloring constituents of rocks and soils, which almost always owe their green, red, or brown colors to pigments containing iron. Iron is a constituent of *hæmoglobin*, the pigment of the red blood cor-

puscles of animals. The human body as a whole contains 0.004 per cent of iron, which in a person of average weight amounts to $\frac{1}{10}$ oz. of the metal.

From these facts it follows that iron compounds are necessary in the diet, which should supply at least 0.015 gram of iron per day. Less than this leads to anæmia and weakness. Among foods rich in iron are lean meat, eggs, oatmeal, raisins, peas, beans, spinach, and green vegetables in general. Foods made from the whole wheat kernel contain abundant iron, but in the making of white flour the iron compounds are mostly removed.

THE IRON AND STEEL INDUSTRY

532. Ores of iron. The chief ores of iron are the following three minerals, of which the first, especially in the United States, is by far the most important:

1. **Hematite**, which is *ferric oxide*, Fe_2O_3 . It occurs in hard, lustrous crystals, which vary in color from red to grayish-black but which always yield a red powder and a red *streak* when drawn across an unglazed porcelain plate. Hematite occurs in enormous deposits in northern Michigan, Wisconsin, and Minnesota, near Lake Superior. More than 50,000,000 tons of hematite are mined annually in this region. Much hematite is also obtained in Alabama, near Birmingham.

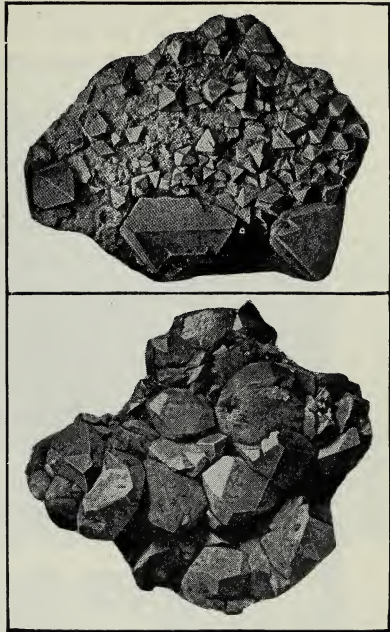
2. **Magnetite**, Fe_3O_4 , occurs in black crystals which yield a black powder and a black streak on a porcelain plate. Unlike hematite, magnetite is attracted by the magnet, and some specimens are naturally magnetic. Large deposits of magnetite are found in the Adirondack region of northern New York, in Sweden, and elsewhere.

3. **Limonite**, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, forms amorphous masses of a yellow or brown color and is used as an excellent and durable paint under the names "ocher" (yellow) and "umber" (brown). It is an important iron ore in Connecticut, Penn-

sylvania, Alabama, and West Virginia, and in Scotland, France, and Germany.

533. Varieties of iron.

Most metals are prepared for use in as pure condition as is possible without too great expense. But iron is an exception. Pure iron is about as soft as aluminum and is not as tough as commercial iron. The iron that is used for structural purposes is prepared by processes which introduce into it a special impurity, *carbon*, which greatly increases the hardness and toughness of the metal. Toughness or tenacity, called *tensile strength* by the engineer, is measured by the force required to pull apart a bar 1 sq. in. in cross section. The effect of carbon upon the tensile strength of iron is shown in the following table:



Courtesy of the U. S. National Museum.

Fig. 246. Crystals of magnetite (above) and hematite (below).

Percentage of Carbon	Tensile Strength, pounds per square inch
0 (pure iron).....	34,000
0.18.....	61,000
0.22.....	65,000
0.50.....	90,000

According to the percentage of carbon and the process of

manufacture, commercial varieties of iron can be divided into three classes:

1. Metal containing 2 per cent or more of carbon. *Cast iron*
2. Metal containing from 2 per cent to 0.1 per cent
of carbon. *Steel*
3. Metal containing less than 0.1 per cent of carbon. *Wrought iron*

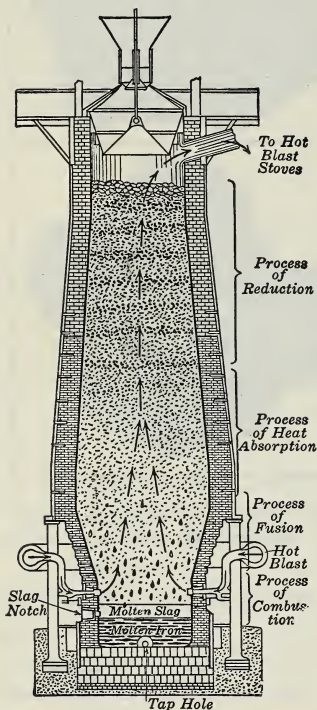


Fig. 247. Diagram of the iron blast furnace.

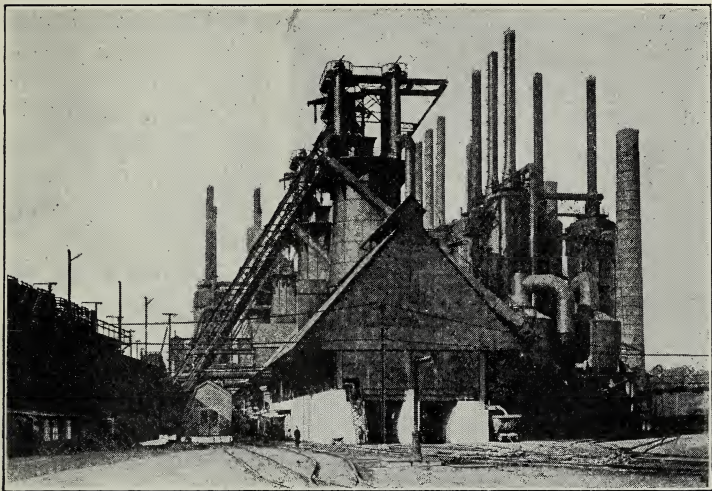
534. Cast iron. Cast iron is made by the reduction of iron ore with carbon in the *blast furnace* (Fig. 247), a round tower about 80 ft. high and 20 ft. in diameter at its widest part, built of steel lined with firebrick. Around the furnace, close to the bottom, are set 10 nozzles called *tuyères* through which blowing engines force a blast of air which has been heated to 800°.

The charge is introduced at the top into a cup-shaped cavity closed below by a cone which can be lowered to allow the material to fall into the furnace. Iron ores consist chiefly of iron oxide, and the carbon, which is almost always used in the form of *coke*, is added for the purpose of removing the oxygen in the form of carbon dioxide and liberating the iron. In addition to the iron ore and coke, *limestone* is charged into the

furnace. This is added as a *flux* to melt down with the earthy and clayey impurities of the ore and form a glassy *slag*, which

collects as a liquid layer above the denser melted iron and protects it from being re-oxidized by the hot oxygen of the blast.

At the tuyères oxygen is abundant, and the coke burns to

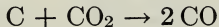


Courtesy of the Bethlehem Steel Co.

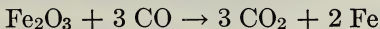
Fig. 248. A blast-furnace plant.

From left to right are shown the ore, coke and limestone bins; the charging conveyors; a ladle receiving molten pig iron; the blast furnaces; a slag ladle; and the stoves for heating the furnace blast.

carbon dioxide, which, as it passes upward through the incandescent coke, is reduced to *carbon monoxide*:

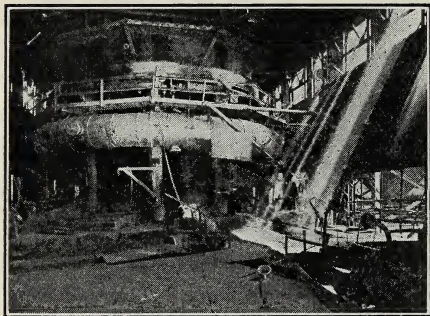


The carbon monoxide reduces the iron oxide of the ore to metal:



and the liberated iron melts and trickles down to the bottom of the furnace, where it forms a layer beneath the slag.

The melted iron is tapped off every six hours, the glowing metal being received in a great ladle, and it may be taken to the steel works for direct conversion into steel. If cast iron is



Courtesy of the Bethlehem Steel Co.

Fig. 249. Tapping the blast furnace.

desired, the liquid metal is cast into sand moulds or iron moulds carried on an endless chain in a "casting machine," and the iron is thus obtained in bars which are known as "pig iron."

Cast iron is the variety employed in an iron *foundry*, where the pig iron is melted for use in a furnace called

a *cupola*. As the name indicates, objects made of it are *cast*, that is, the iron is melted, poured into a sand mould, and there allowed to solidify. Cast iron cannot be welded, forged, or tempered. It resists rust much better than steel, but it is hard and rather brittle, and it is unsuited for objects that are to be exposed to shock or to great stress. It is used for gas and water mains, stoves, radiators, the frames of machines of many kinds, etc.

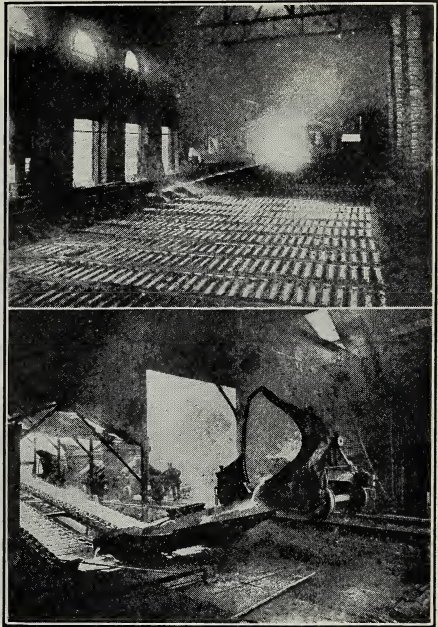
The principal impurities in commercial cast iron are the following:

Carbon	2.5 to 4 per cent
Silicon	} Variable amounts depending upon the composition of the ore, coke, and limestone charged into the blast furnace
Manganese	
Sulphur	
Phosphorus	

535. Wrought iron. Wrought iron is made from cast or pig iron by removing the impurities just mentioned by oxida-

tion, a process which is known as "*puddling*." The hearth of a reverberatory furnace is lined with iron oxide, and the charge of bars of pig iron is broken up and piled upon it. The metal is then melted and vigorously stirred with an iron bar for an hour. During this time bubbles of carbon monoxide, formed by the combination of the carbon of the pig iron with the oxygen of the iron oxide, escape, so that the metal appears to boil. The sulphur escapes as sulphur dioxide, while the silicon, manganese, and phosphorus combine with oxygen, leave the iron, and pass into the slag.

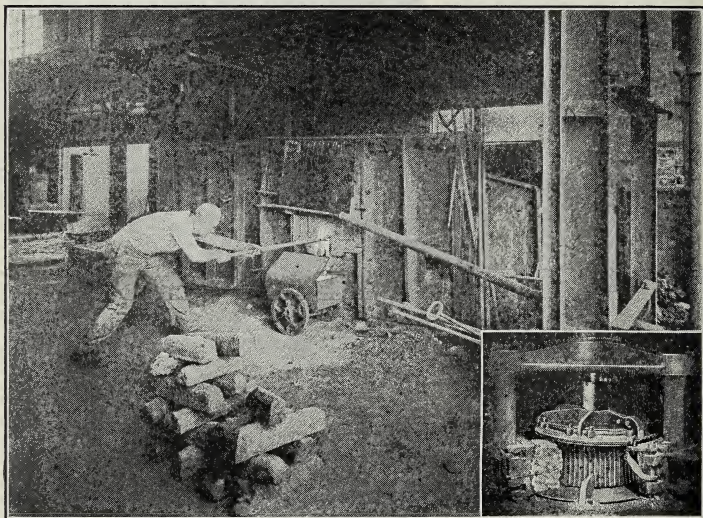
When this purification is almost complete, the liquid sets to a pasty mass, because the melting point of wrought iron is much higher than that of cast iron. When this stage is reached, the puddler takes an iron paddle and works the charge into balls weighing about 150 lb., which are compressed in a rotary squeezer to expel the slag and then rolled out into long bars. To obtain the best quality of wrought iron these bars are cut up, arranged into bundles, reheated and rolled again, and the rolling repeated a third time.



Photographs from Chicago Architectural Photo. Co.

Fig. 250. Old and modern methods of pig casting: above, sand casting; below, machine casting.

The finished product contains 0.1 per cent or less of carbon and small percentages only of silicon, manganese, sulphur, and phosphorus. It is quite tough, though less so than the best steel, and it is even more easily welded and forged than the latter. Wrought iron cannot be tempered. It resists rust far better than does steel, but wrought iron is more expensive to produce, so that steel is displacing it for many purposes.



Courtesy of the Reading Iron Co.

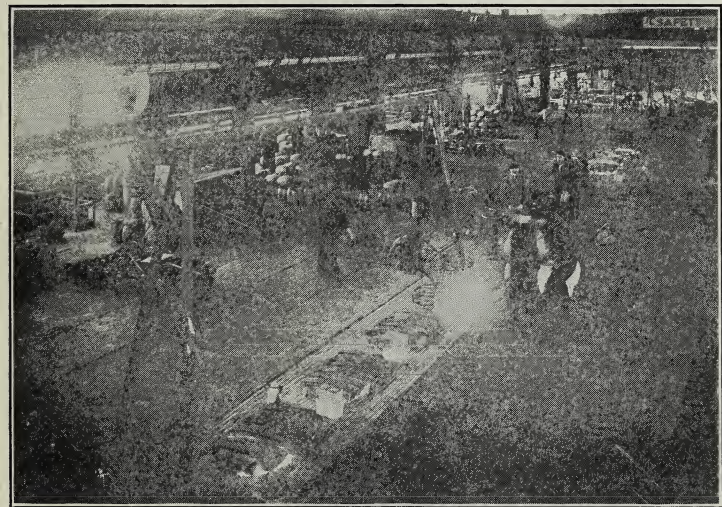
Fig. 251. Working up the ball in the puddling furnace. Inset: the ball in the rotary squeezer.

Wrought iron is used for pipe, nails, chains, bolts, wire, fencing, horse shoes, etc.

536. Steel. Commercial steel contains from 0.1 per cent to 1.5 per cent of carbon. One-quarter of 1 per cent of carbon produces a tough, soft, "mild" steel which will not hold a cutting edge, while 1.2 per cent yields a hard, brittle steel suitable for files or razors.

Steel also contains variable amounts of silicon and manganese, which are not to be considered harmful impurities and are, indeed, often purposely introduced. Steel high in silicon is used for springs, and high-manganese steel is intensely hard and tenacious.

Phosphorus and sulphur have a purely harmful effect. Phosphorus makes the steel brittle while cold ("cold short"),



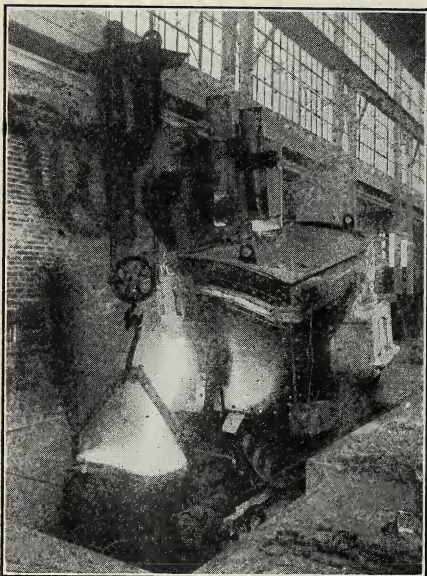
Courtesy of the Halcomb Steel Co.

Fig. 252. Melting floor of a crucible steel plant, showing tops of the gas-fired regenerative crucible furnaces.

and sulphur makes it brittle while hot ("red short"), so that it is impossible to weld, forge, or roll a steel high in sulphur. One-tenth of 1 per cent of phosphorus or sulphur is above the permissible limit in a steel rail, whereas 0.05 per cent of either would cause the rejection of a steel intended for boiler plates. For armor plate or high-grade cutlery, 0.03 per cent of phosphorus or sulphur is the limit.

In percentage of carbon, steel is intermediate between cast iron and wrought iron. This fact is the basis of the different methods of converting cast iron and wrought iron into steel:

1. Wrought iron is heated in contact with powdered charcoal until the iron absorbs the amount of carbon required to change it into steel.



Courtesy of the "Scientific American."

Fig. 253. An electric furnace for high-grade steel.

This is the **cementation process**, by which high-grade tool steel is made.

2. Cast iron is melted with iron oxide, as in making wrought iron, but not all the carbon is removed. Small portions of the metal are withdrawn from time to time and rapidly analyzed, and when the percentage of carbon has fallen to the desired figure, the liquid steel is drawn off into a ladle. This is the **open-hearth process**.

3. By blowing air through melted cast iron *all* the carbon is burned out, and when this has been accomplished, the proper amount of spiegeleisen rich in carbon is added to bring the carbon back again to the required percentage. This is the **Bessemer process**.

537. The cementation process. The furnace in which the cementation process is carried out contains two long fire-clay boxes, each of which accommodates 5 tons of bars of high-

grade wrought iron, packed in charcoal powder. When the furnace is fired, flames envelop these boxes, which are kept at a bright red heat for a week. Then the furnace is allowed to cool, and the bars of steel are broken up and melted in crucibles to obtain a metal of uniform composition. A large proportion of the high-grade steel for cutlery is now made in small electric furnaces.

Steel made from wrought iron by these and similar methods is called **crucible steel**. It contains from 0.8 to 1.5 per cent of

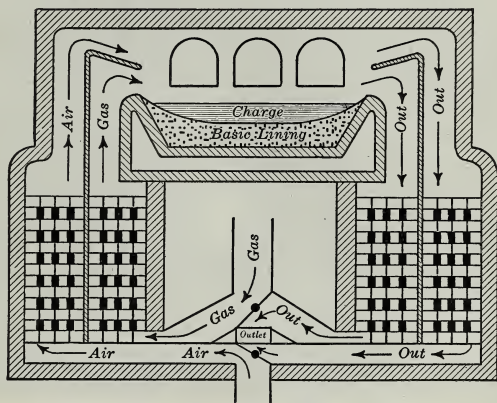


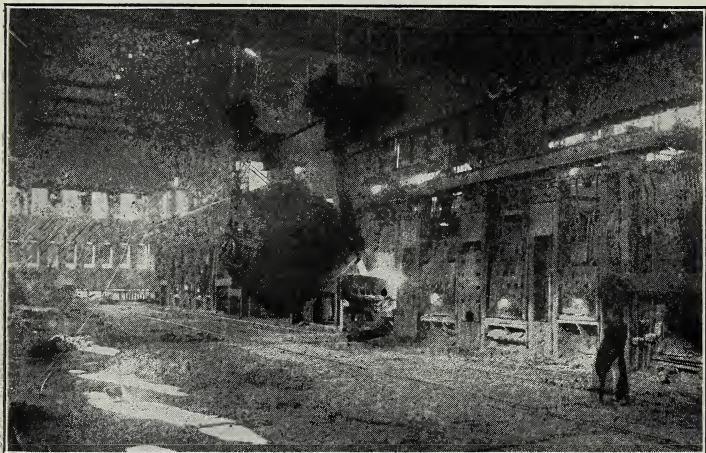
Fig. 254. The regenerative open-hearth furnace.

carbon. It is expensive and is used for small objects in which quality is the first consideration, such as watch springs, needles, surgical instruments, pens, tools, knives, razors, scissors, and other cutlery.

538. The open-hearth process. A vertical section of the open-hearth furnace is given in Figure 254. The **regenerative system** of heating should be noted. The fuel gas passes through a checker-work of red-hot fire brick on its way to the hearth, and the air necessary for combustion is pre-heated in the same way. Thus fuel is saved and a temperature of $1,500^{\circ}$ obtained,

which could scarcely be reached by the use of cold gas and cold air.

On their way out of the furnace the products of combustion pass through two similar checker-works, which in about half an hour become heated to a bright red heat. By means of valves the direction of the gas and air is then reversed. The fuel gas passes through one of the red-hot checker-works and



Courtesy of the U. S. Steel Corporation.

Fig. 255. Charging an open-hearth furnace; the four ports in the foreground all belong to one furnace.

the air through the other, while the other two systems are now heated by the products of combustion from the furnace.

The hearth of the furnace is 40 ft. long, 12 ft. wide, and 2 ft. deep. It is lined with bricks made of a mixture of lime and magnesium oxide, and it will hold 100 tons of liquid metal. The charge consists of scrap steel awaiting utilization, molten pig iron from the blast furnace, and hematite, Fe_2O_3 , to oxidize the impurities of the cast iron. *Lime* is also added, with the important object of causing the phosphorus and sulphur of

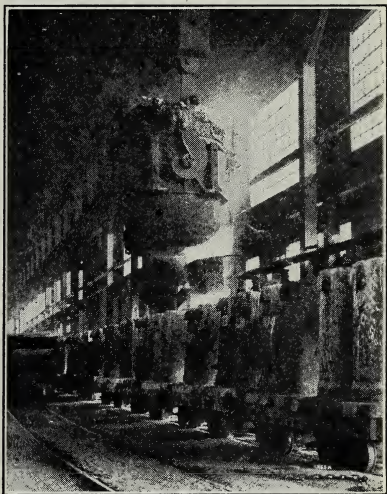
the charge to leave the melted metal and enter the slag as calcium phosphate and calcium sulphate.

After being heated for about 8 hours, the carbon has usually fallen to the desired percentage, and the melted steel is tapped into a ladle containing a little ferro-manganese, which favors the formation of a sound casting. From the ladle the steel is cast into ingot moulds.

In the United States the open-hearth process annually produces a much larger tonnage of steel than does any other process. Open-hearth steel is used for machinery, heavy guns, armor plate, rails, bridge members, girders, boiler plates, and countless other purposes.

539. The Bessemer process. The Bessemer process is carried out in a *converter* (Fig. 183), which is like a great egg-shaped ladle, 15 ft. high by 8 ft. in diameter, swung so as to turn in a vertical plane. It is lined with refractory brick rich in silica, and it has a false bottom containing numerous $\frac{1}{4}$ -in. perforations through which air under pressure can be forced through the contents of the converter.

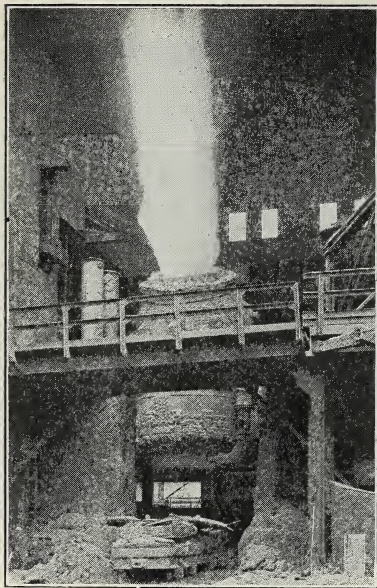
Fifteen tons of molten pig iron from the blast furnace are placed in the converter, and the blast turned on for 15 minutes. A long bright flame rushes from the mouth of the vessel as the carbon of the cast iron burns to carbon dioxide, while the silicon and manganese also oxidize and enter the slag.



Courtesy of the Bethlehem Steel Co.

Fig. 256. Casting steel ingots in ingot moulds.

Unfortunately the sulphur and phosphorus are not affected. When the oxidation is finished, enough spiegeleisen is added to the converter to bring the carbon to the desired percentage, 0.3 to 0.5 per cent. The metal is then cast into ingots.



Courtesy of The U. S. Steel Corporation.

Fig. 257. Bessemer converter in action.

charge of melted cast iron. As in the open-hearth process, the lime causes the phosphorus and sulphur to leave the metal and enter the slag. The basic Bessemer process is not employed in the United States, but it is of great importance in steel making in Europe.

540. Temper. When a blade made of high-carbon steel (crucible steel) is heated red-hot and quenched in water, it becomes as hard and almost as brittle as glass. If heated once more and allowed to cool *slowly*, the steel is softened

Bessemer steel is somewhat too high in phosphorus and sulphur for uses involving great stress or shock. It is employed for steel pipe, corrugated roofing, and steel plate that is to be tinned for roofing or for cans for preserving food products. The Bessemer tonnage is decreasing, as open-hearth steel is taking the place of Bessemer for purposes other than those just mentioned.

The **basic Bessemer process** is identical with the process just described, except that the converter is lined with bricks made of lime and magnesium oxide, and lime is added with the

to an extent depending upon the temperature of the second heating. This is called "drawing the temper." Thus the hardness of steel can be changed at will by heat treatment, and the importance of the fact in fitting steel for various uses is plain, for the most different tools can be made of the same metal and afterward finished either hard and brittle or soft and tough by reheating the quenched objects to different temperatures. The reheating is done in a gas-fired furnace, the temperature of which is carefully measured and controlled. A few indications of the most suitable reheating temperatures for various objects are given below:

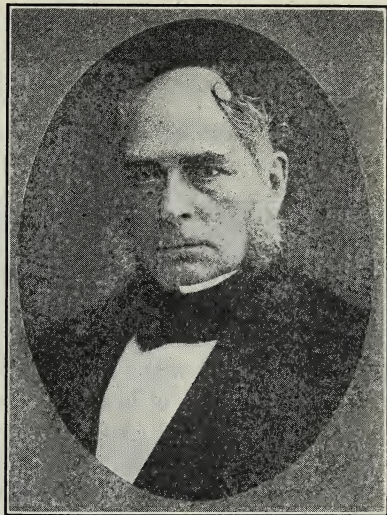


FIG. 258. SIR HENRY BESSEMER
(1813-1898).

English metallurgist and steel maker; invented the Bessemer process of steel making and other minor metallurgical processes.

Razors, files, surgical instruments.....	220°
Penknife blades.....	240°
Chisels, gouges, plane cutters.....	260°
Axes, table cutlery, springs.....	270°
Wood saws.....	300°

541. Special steels. The special or alloy steels that contain notable quantities of other metals have been mentioned. A tabular summary of some of the more important is given here:

Chromium, 1 per cent.....	Balls and rollers for bearings
Chromium, 2 per cent.....	Burglar-proof safes, motor-car gears

Nickel, 3.25 per cent	Bridges, gun forgings, motor-car parts
Nickel, 3.25 per cent; chromium, 1.5 per cent	Armor plate, projectiles
Chromium, 4.5 per cent; tungsten, 18 per cent; vanadium 0.6 per cent	High-speed tool steel (§ 503)
Tungsten, 6 per cent	Permanent magnets
Manganese, 8 per cent to 14 per cent	Burglar-proof safes, jaws of rock crushers, railway frogs
Vanadium, 0.1 per cent	Motor-car parts

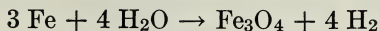
542. The iron output. In 1800 the annual iron production of the world was only 830,000 tons. At present the United States alone produces 42,000,000 tons, while the total annual production of the world is about 90,000,000 tons. If the world's annual production of iron were forged into a bar 6 in. wide by $\frac{1}{2}$ in. thick, it would girdle the earth at the equator 125 times. Rolled into a sheet 1 in. thick, it would form a roadway 250 ft. wide stretching across the United States from the Atlantic to the Pacific. Each minute of the day and night 326,000 lb. of iron is produced. Although iron is the cheapest of the metals, yet the total value of the iron output is $1\frac{1}{2}$ times as great as that of all of the other metals together, the precious metals included.

543. The rusting of iron. Dry air does not affect iron, but in presence of moisture the metal becomes covered with a reddish-yellow layer of **rust**, which contains ferric oxide and water and has the same composition as limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The layer of rust is porous and does not protect the iron beneath, so that the oxidation continues until the metal is completely disintegrated (Fig. 22).

The rusting of iron causes great loss and damage, and many efforts have been made to prevent it. The earliest plan, which is still the most important, was the use of *protective coatings*. Iron is plated with zinc, tin, copper, and nickel chiefly to render

it rustproof. Covering iron and steel with paints containing red lead, zinc chromate, and other pigments is another way of arriving at the same result.

When an iron object is heated to redness in a chamber through which steam is passed, hydrogen is liberated, and a film of the magnetic iron oxide, Fe_3O_4 , is formed on the surface:

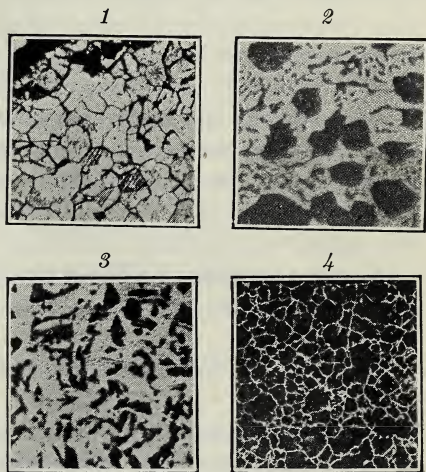


The black coating thus obtained adheres strongly to the iron and prevents it from rusting. Iron which has been protected in this way is known as "**Russia iron.**"

Iron that is free from carbon and from the other impurities usually present rusts far less rapidly than ordinary iron and steel. By a special modification of the open-hearth process, iron of almost 100 per cent purity is now made commercially on a large scale and sold under the name "**ingot iron.**" Such iron is far less tenacious than steel, but it has a wide and varied field

of usefulness, simply on account of its resistance to rust.

Iron or steel treated with *phosphoric acid* under proper con-



Courtesy of Prof. William Campbell.

Fig. 259. Photomicrographs of the internal structure of irons and steels of various carbon contents.

Microscopic study of metals, the science of *metallography*, reveals much as to physical properties and the effects of heat treatment. The above specimens are: 1, wrought iron, showing crystals of pure iron and slag inclusions; 2, white cast iron; 3, structural steel; and 4, high-carbon steel, all enlarged 50 diameters.

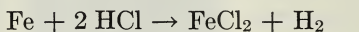
ditions becomes covered with a rustproof layer of iron phosphate. In this way submarine mines were rustproofed during the World War, and the process is extensively used for other purposes.

Copper, unlike other impurities, *retards* the rusting of iron and steel. Corrugated steel roofing containing 0.25 per cent of copper resists the weather more than twice as long as does ordinary steel under the same conditions.

COMPOUNDS OF IRON

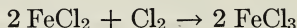
544. Ferrous and ferric compounds. Iron forms two series of compounds, the **ferrous** compounds, in which the iron is *bivalent*, and the **ferric** compounds, in which the iron is *trivalent*. Ferrous chloride and ferric chloride will serve as types of the two series:

Ferrous chloride, FeCl_2 , is obtained by dissolving iron in hydrochloric acid:



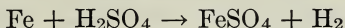
The green crystals which separate when the solution is evaporated possess the formula $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ and are freely soluble in water.

Ferric chloride, FeCl_3 , can be obtained by heating iron in chlorine, or by passing chlorine into a solution of ferrous chloride, whereupon the color changes at once from pale green to deep yellow:



Upon evaporation, brown, imperfect crystals separate which possess the formula $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, and are soluble in water and in alcohol. The druggist's "**tincture of iron**" is an alcoholic solution of ferric chloride.

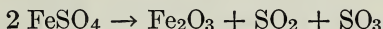
545. Ferrous sulphate, FeSO_4 . Ferrous sulphate results when iron dissolves in sulphuric acid:



Ferrous sulphate is a by-product of the industry. Iron and steel castings are cleaned and freed from scale by soaking them in dilute sulphuric acid, a process which is known as "pickling." When by repeated use the sulphuric acid in the pickle is nearly all converted into ferrous sulphate, the liquid is boiled down with the addition of some scrap iron until crystals of ferrous sulphate separate on cooling.

Ferrous sulphate forms transparent, green crystals of the formula $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, which have long been known as **green vitriol** or **copperas**. It is used as a mordant in dyeing and calico printing, as a disinfectant, and in the manufacture of ink.

When ferrous sulphate is heated to redness in a reverberatory furnace, it leaves a residue of ferric oxide:



The chief use of ferrous sulphate is for the preparation of ferric oxide in this way, the ferric oxide being employed as a red pigment and as a polishing powder.

546. Ink. When a solution of ferrous sulphate is mixed with a solution of *tannic acid*, **ferrous tannate** is formed. Since ferrous tannate is colorless and soluble in water, the liquid does not change its appearance. If, however, the solution is exposed to the air, oxidation takes place, and **ferric tannate**, which is deep black and insoluble, appears as a finely divided precipitate suspended in the liquid.

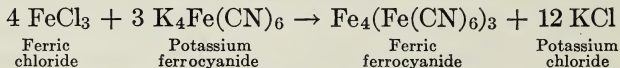
This behavior is the basis of the manufacture of the best grades of black ink. **Nut galls**, which are round lumps produced on the twigs of oak trees by the bite of the gall fly, are rich in tannic acid, and the solution of tannic acid is made by

digesting crushed nut galls with water and filtering. This is then mixed with ferrous-sulphate solution. Since it is inconvenient to write with a colorless liquid, a little blue or green coal-tar dye is added to make the writing visible when the ink is fresh. A little hydrochloric acid improves the keeping qualities, and for the same reason a trace of some antiseptic, such as mercuric chloride, is introduced. A small quantity of dextrin or of some other gum is added to thicken the ink slightly and prevent the ferric tannate from settling.

547. Potassium ferrocyanide, $K_4Fe(CN)_6$. Potassium ferrocyanide is a by-product of the manufacture of illuminating gas, being obtained from the mass left in the purifier after the iron ore is saturated with impurities absorbed from the gas. It can also be obtained by heating nitrogenous organic matter, such as chips of leather or horn, in a crucible with iron filings and potassium carbonate. The black fused mass is crushed and extracted with water, and the filtered solution evaporated till the potassium ferrocyanide crystallizes on cooling.

Potassium ferrocyanide forms lemon-yellow crystals, which contain 3 molecules of water. Unlike the cyanides, it is not poisonous. Its chief use is for the preparation of the important pigment **Prussian blue**.

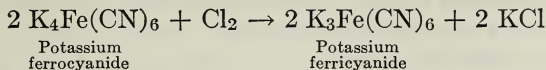
548. Prussian blue, $Fe_4(Fe(CN)_6)_3$. When a solution of potassium ferrocyanide is mixed with one of ferric chloride, a deep-blue precipitate of *ferric ferrocyanide*, commonly called **Prussian blue**, is formed:



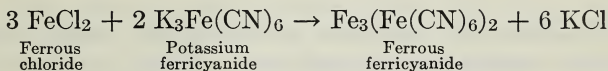
Ferric ferrocyanide is extensively used as a pigment in paint, in dyeing, in coloring paper, and in bluing garments after washing.

549. Potassium ferricyanide, $K_3Fe(CN)_6$. When chlorine gas is passed into a solution of potassium ferrocyanide, the color of the liquid deepens, and when the liquid is evaporated

and cooled, garnet-red crystals of potassium ferricyanide, $K_3Fe(CN)_6$, are deposited:



Potassium ferricyanide gives *no precipitate* with a solution of *ferric* chloride, but with a solution of *ferrous* chloride it yields a deep-blue precipitate of *ferrous ferricyanide*, known as **Turnbull's blue**:



550. Blueprinting. Blueprint paper is coated with a solution containing *potassium ferricyanide* and *ferric ammonium citrate* and dried in the dark. Exposure to light converts the ferric salt into ferrous salt, which interacts with the potassium ferricyanide, forming ferrous ferricyanide, and turning the paper *blue*. If during the exposure the paper is covered with a drawing made in black ink on a transparent fabric, the lines will protect the paper from the light, and the drawing will appear in white on a blue ground. The only fixing necessary is washing with water, which removes the sensitive coating and makes the drawing permanent. The "ink" used for writing in white on a blue print is a solution of sodium hydroxide, which dissolves and decolorizes ferrous ferricyanide.

NICKEL (Ni = 58.7)

551. Occurrence. Nickel is obtained chiefly from the Sudbury district in Ontario, Canada, and from New Caledonia. The Sudbury ore is iron sulphide containing 5 per cent of its weight of nickel; that of New Caledonia is a silicate of magnesium and nickel known as **garnierite**.

552. Properties. Nickel is a white metal which when polished has a brilliant lustre. Its density (8.9) is higher, and its melting point ($1,432^{\circ}$) a little lower, than the corresponding figures for iron, which it resembles in many respects. Like iron, it is malleable, ductile, and tenacious, and it is attracted by the magnet.

In chemical conduct nickel is much less active than iron. It scarcely rusts in moist air, and even at a red heat its combination with oxygen takes place slowly. It is not rapidly attacked by hydrochloric or sulphuric acid but dissolves readily in nitric acid.

553. Uses. An important application for nickel is as a protective coating for iron and steel. Nickel can be *welded* with steel, and culinary utensils are often made of sheet steel on both sides of which a thin plate of nickel has been welded. More usually, steel is *electroplated* with nickel by making the steel object the cathode of a low-voltage direct current in a solution of *nickel ammonium sulphate*, the anode being a bar of pure nickel.

A small percentage of nickel greatly increases the tenacity of steel. Steel containing 3.25 per cent of nickel is largely used for gun forgings, machinery, automobile parts, and in general where the stress is too severe for ordinary steel. Steel containing 3.25 per cent of nickel and 1.5 per cent of chromium is hard as well as tough and is used for armor plate.

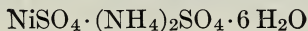
Percentages of nickel ranging from 22 to 30 make steel rustproof and almost non-oxidizable when heated. Such alloys are used in the valves and spark plugs of gasoline motors, in the valves of the salt-water fire-protection service of New York City, in the tubes of marine boilers, and, in the form of wire, in electric irons, heaters, toasters, and cooking utensils.

Another interesting property of this high-nickel steel is the fact that its expansion when heated is as small as that of glass, so that if glass is softened by heat and a wire made of high-nickel steel is pushed through it, the joint will remain airtight

when cold. This is turned to account in the incandescent lamp, in which the electric current is carried through the glass into the vacuum and out of it by two wires of high-nickel steel. Steel containing 36 per cent of nickel is called **invar**. This material scarcely expands at all when heated. It is used for surveyors' tapes, which, when made of it, have the same length at all temperatures. Invar has been tried for the pendulum rods of clocks and for the balance wheels of watches, but it did not prove as satisfactory as the compensation devices previously in use.

Of the *alloys* of nickel, **German silver** has been mentioned under copper. Nickel has a remarkable decolorizing action upon copper, so that the nickel coins, which contain but 25 per cent of nickel and 75 per cent of copper, show no trace of the color of the latter metal. "**Monel metal**" is an alloy of copper and nickel with a little manganese. It is hard, tenacious, rustproof, oxidizes very slowly when heated, and resists well the corrosive action of many solutions. Monel metal has a wide field of usefulness for constructive purposes and in chemical engineering.

The most important *compound* of nickel is *nickel ammonium sulphate*. It is obtained by mixing concentrated solutions of nickel sulphate and of ammonium sulphate; dark-blue crystals separate which correspond to the formula



Nickel ammonium sulphate is employed in electroplating with nickel.

COBALT (Co = 59)

554. Properties and uses. Cobalt occurs with nickel in nature and resembles it closely, being a white, malleable, magnetic metal, capable of taking a high polish. Its lustre is permanent in the air. Cobalt can be electroplated on steel

even more readily than can nickel, and the plating is indistinguishable from nickel plating. The only hindrance to this application is the higher price of cobalt.

Some of the alloys of cobalt have properties which are bringing them into extensive use. The alloy of 80 per cent of cobalt with 20 per cent of chromium resembles silver in appearance, does not tarnish, and is as hard and tenacious as good crucible steel. Since it is unaffected by moisture and by the acids present in food products, it is an ideal metal for the manufacture of table knives, forks, and spoons.

"Stellite" contains 55 per cent of cobalt, 35 per cent of chromium, and 10 per cent of tungsten. The valuable property of this alloy is its intense hardness, which it retains even when heated and allowed to cool slowly. It is used to some extent instead of high-speed tool steel in machining steel and cast iron.

555. Compounds of cobalt. Cobalt chloride, CoCl_2 , forms red crystals of the formula $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, which when heated become deep blue, changing to the anhydrous salt CoCl_2 . The water solution of cobalt chloride, which is a pale-pink liquid, is employed as **sympathetic ink**. Characters written with it are invisible, but when the paper is warmed, the water is vaporized, and the intensely blue CoCl_2 is formed, so that the message appears in blue letters, which if exposed to moist air, will again disappear because the CoCl_2 absorbs water from the air.

The important blue pigment **smalt** is *potassium cobalt silicate*, made by melting cobalt oxide and potassium carbonate with white sand. The glassy blue mass is broken up by plunging it while hot into water and then finely powdered for use. The great merit of smalt is the fact that its fine blue color is unaffected by light, by the weather, and by acids. It is used in paint and for neutralizing the yellow tint in the finest grades of paper, especially ledger paper.

PLATINUM (Pt = 195)

556. The Platinum Family. The Platinum Family is composed of six dense, grayish-white, *noble* metals which are found together in nature. They are unaffected by oxygen at any temperature, retain their lustre permanently in the air, and dissolve only in aqua regia. **Osmium** must be mentioned because it is the densest of all substances (specific gravity 22.5) and one of the most difficult to melt. **Iridium** is of interest on account of its use to harden platinum. The tips of gold pens are made of an alloy of platinum and iridium, and the same material is employed for government standards of weight and length.

557. Occurrence of platinum. Platinum occurs in dense, shining, silvery scales in some river sands of the Ural Mountains and of Colombia and Brazil. The scales contain about 80 per cent of platinum, which is alloyed with the five other metals of the platinum family and with copper and iron.

558. Properties. Platinum is a gray metal with a high lustre, which is permanent in dry or moist air even at a red heat. Its specific gravity is 21.5, which is nearly twice that of lead and greater than that of gold. Platinum is, therefore, the densest of the *familiar* metals. It is somewhat harder and more tenacious than gold, and only gold and silver surpass it in malleability and ductility. The melting point of platinum ($1,755^{\circ}$) is far above a white heat. When sufficiently heated, it can be forged and welded, a property which is turned to account in making platinum vessels for the laboratory.

559. Chemical conduct. Platinum is a *noble* metal, and its chemical conduct is similar to that of gold. It is not affected by air or water at any temperature. Its compounds are not numerous, and they are all easily decomposed by heat, leaving a residue of platinum in a black, finely divided, spongy form. The three ordinary acids have no effect upon platinum, but it dissolves slowly in aqua regia.

Finely divided platinum is a *catalyst* of remarkable power, especially for chemical changes in which gases take part. The **Dobereiner lamp** consists of a hydrogen generator in which a pellet of spongy platinum is supported in such a position that the escaping hydrogen is directed against it. The combination of the hydrogen with the oxygen of the air takes place with such energy at the surface of the platinum that the latter glows and the hydrogen is ignited.

560. Uses. Because of its high melting point and its chemical inactivity, platinum is made into crucibles, dishes, foil, wire, and electrodes which are indispensable to the chemist. On a large scale it is largely used as a catalyst, often in the finely divided form known as **platinum black**, which is usually coated on asbestos, as in the manufacture of sulphuric acid by the contact process. The use of platinum gauze in making nitric acid from ammonia is another application of the catalytic activity of the metal. Another instance is the **self-lighting gas mantle**, in the upper part of which is suspended a pellet of spongy platinum which glows when the gas is turned on, and produces ignition. The principle is that of the Dobereiner lamp, for illuminating gas contains half its volume of hydrogen. Pocket cigar lighters using alcohol as a fuel make similar use of this property of platinum.

Platinum, being quite unaffected by the liquids of the mouth, is suitable for dental uses and is employed for the supporting pins of pivot teeth and bridge work and for many other purposes. Considerable quantities of platinum are consumed in tipping the nickel-steel wires used in the spark plugs of gasoline motors.

Platinum is now being largely employed for jewelry, especially for chains and for settings. For this purpose of mere personal adornment it has no advantage over other white metals and alloys, but the increased demand thus produced has raised the price of platinum until it has become 5 times as expensive as gold, and has made it difficult for the chem-

ical industries to obtain this indispensable metal for their work.

SUMMARY

The **ores of iron** are *oxides*. They are reduced in the blast furnace with coke, limestone being added as a flux. The product is **pig iron** which serves in turn as the raw material for wrought iron and steel.

Cast iron contains over 2 per cent of *carbon* and variable amounts of *silicon, manganese, sulphur, and phosphorus*.

Wrought iron contains less than 0.1 per cent of carbon and only traces of the other four impurities.

Steel contains from 0.1 per cent to 2 per cent of carbon. It can be *cast, forged, welded, and tempered*. Silicon and manganese do not injure steel. Sulphur and phosphorus are harmful.

Steel for cutlery and tools is made by the **cementation, crucible, or electric furnace** process.

Steel for girders, rails, guns, armor plate, boiler plates, etc., is made by the **open-hearth process**.

Low-grade steel requiring no great strength for cans, culinary utensils, roofing, water pipes, etc., is made by the **Bessemer process**.

In the **ferrous** salts the iron atom is *bivalent*; in the **ferric** salts it is *trivalent*.

Important iron compounds are:

Ferrous sulphate.....	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$
Potassium ferrocyanide.....	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$
Prussian blue.....	$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$
Potassium ferricyanide.....	$\text{K}_3\text{Fe}(\text{CN})_6$
Turnbull's blue.....	$\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$

Nickel resembles iron. Its chief uses are for plating on steel and for making nickel steel.

Cobalt is similar to nickel and could be used instead of it for many purposes if a cheaper supply of cobalt were available.

EXERCISES

1. Why is metallic iron rare in nature although the compounds of the metal are so abundant? Explain the occurrence of native iron in meteors.
2. Enumerate some methods of rustproofing iron.
3. Steel table knives that are to remain unused for some time are frequently smeared with oil or vaseline. Why?
4. How could you ascertain whether a solution contained a ferrous or a ferric salt?
5. Why is limestone added in the blast-furnace process?
6. What are the reasons for the great industrial importance of blueprints?
7. Wrought iron was known to prehistoric man, but cast iron was first produced about the date of the discovery of America. Why?
8. Trace the effect of increasing the percentage of carbon upon the properties of iron.
9. Wrought iron is more expensive and less tenacious than steel. Why does it remain in use?
10. Make a tabular comparison of iron, cobalt, and nickel.
11. Enumerate four useful alloys of nickel.
12. Why is the Bessemer process receding and the open-hearth process advancing?
13. Make in the form of a table a comparison of platinum and gold.
14. What properties of platinum fit it especially for the purposes of the chemist? Would gold answer as well?
15. What would be the increase in weight of 30 grams of iron if converted into ferric oxide?
16. How many grams of iron are there in 100 grams of (a) magnetite, (b) hematite, (c) limonite?
17. How many times denser is platinum than hydrogen gas? Take the weight of 1 liter of hydrogen as 0.09 gram.
18. Uranium has the highest *atomic weight* of all the elements, but osmium has the highest *specific gravity*. Explain exactly what this statement means. Is there any contradiction in it?

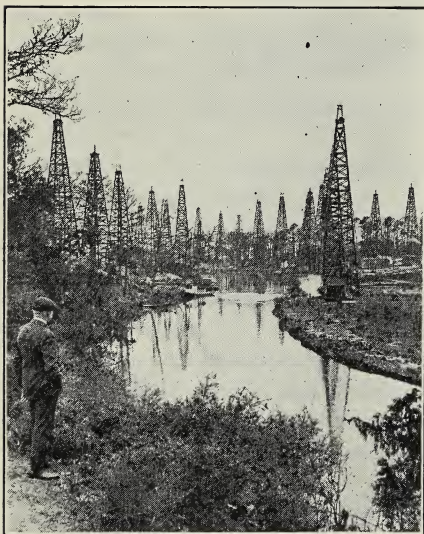
REVIEW QUESTIONS

1. Compare the rusting of iron, copper, zinc, lead, and aluminum.
2. Would it be an advantage or a disadvantage if iron *followed* hydrogen in the electromotive series instead of preceding hydrogen?
3. Write formulas showing the arrangement of the atoms in the molecules of methane, ethane, and propane.
4. About how many compounds of carbon are known? What peculiarity of the carbon atoms is responsible for the enormous number of carbon compounds?
5. Give the names and formulas of five carbon compounds, not hydrocarbons, that have already been studied.

CHAPTER XL

THE HYDROCARBONS

561. General. The compounds of carbon and hydrogen are called **hydrocarbons**. For the reasons explained in section 268 they are very numerous. *Methane*, CH_4 , the simplest hydrocarbon, has been discussed (§ 289). The present chapter is devoted chiefly to the discussion of a few hydrocarbons of great industrial importance.



Copyright, Ewing Galloway.

Fig. 260. Oil wells in a Texas field.

PETROLEUM

562. Occurrence.

Petroleum, or rock oil, is obtained by drilling wells which vary in depth from 50 to 4,000 ft., the average being about 1,500 ft. To induce or increase the flow of the oil the drilled well is *torpedoed*. This consists in lower-

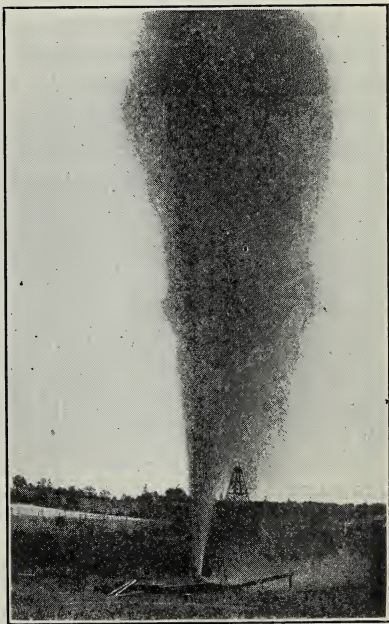
ing into the well a tin case 10 ft. long and 5 in. wide filled with nitroglycerine. The case has a percussion cap and is exploded by dropping a heavy piece of iron into the well.

At first the oil often bursts out of the well with great energy. Many "gushers" have yielded 75,000 barrels¹ per day, and occasional daily yields of 200,000 barrels have been obtained, but the natural flow finally subsides, and it becomes necessary to pump the oil to the surface.

The United States is the chief producer of petroleum, the oil coming mainly from Oklahoma, California, Texas, and Pennsylvania. It is transported by pumping through pipe lines. One pipe line leads through Kansas City and Chicago to the oil refineries at Bayonne, N. J., a distance of 1,600 miles. Important oil fields exist in Mexico and in Russia, but in both countries the industry is crippled by political disorders.

563. Properties. Crude petroleum is an oily liquid lighter than water, on which it floats without mixing. Different samples vary in color from clear brown to greenish-black, and petroleum may have a pleasant ethereal smell or a disgusting odor due to sulphur compounds.

Petroleum is combustible, and when burned it yields 11,000 calories per gram consumed. It is upon this enormous libera-



Courtesy of the "Scientific American."

Fig. 261. The first gush from a torpedoed well.

¹ The barrel of petroleum contains 50 gallons.

tion of energy that the usefulness of petroleum for the most part depends.

564. Chemical composition. Petroleum consists of compounds of *carbon* and *hydrogen*, that is, it is a **mixture of hydrocarbons**. When petroleum is burned, the carbon is oxidized to carbon dioxide and the hydrogen to water. Pennsylvania petroleum consists of a special series of hydrocarbons called the **methane series**, because *methane*, CH_4 , is the first member.

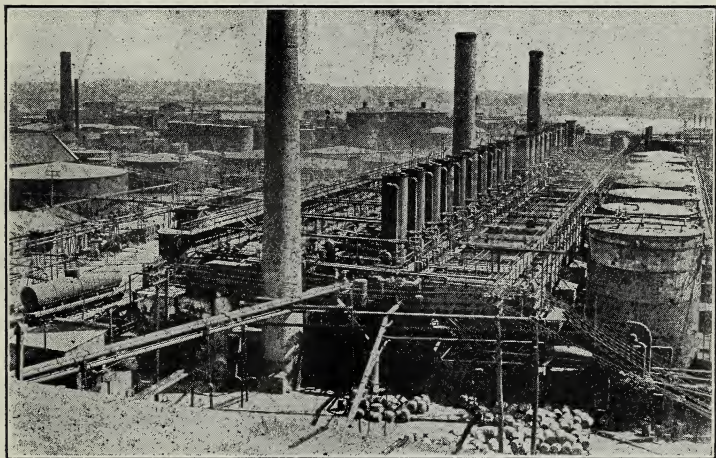
565. The methane series. *In the methane series the number of hydrogen atoms in the molecule can be obtained by multiplying the number of carbon atoms by 2 and adding 2 to the product.* This relation is expressed by the statement that the general formula of the series is $\text{C}_n\text{H}_{2n+2}$. Many members of the series are contained in Pennsylvania petroleum. A partial list follows:

Name	Formula	Physical State
METHANE.....	CH_4	Gas
ETHANE.....	C_2H_6	Gas
PROPANE.....	C_3H_8	Gas
BUTANE.....	C_4H_{10}	Gas
PENTANE.....	C_5H_{12}	Liquid
HEXANE.....	C_6H_{14}	Liquid
* * *	* * *	* * *
EICOSANE.....	$\text{C}_{20}\text{H}_{42}$	Waxy solid
* * *	* * *	* * *
HEXACONTANE.....	$\text{C}_{60}\text{H}_{122}$	Solid

The first four members are gases. The next fifteen are liquids, the simpler ones being volatile liquids with an odor like that of gasoline, while, as we ascend in the series, the liquids become oily and almost odorless. The higher hydrocarbons from $\text{C}_{20}\text{H}_{42}$ upward are colorless, waxy solids, resembling paraffin.

566. Petroleum refining. In refining, the petroleum is allowed to flow into large steam-heated steel cylinders and is

there *distilled*, the vapor being condensed in a coil of pipe surrounded by cold water. A thermometer immersed in the vapor controls the process. At first the gases dissolved in the oil escape, and at 40° liquid begins to collect in the receiver. From this point to 150° the liquid which distills is called **naphtha**. The receiver is then changed, and above 150° the distillate is collected as **kerosene**. Still further increase in



Courtesy of the Atlantic Refining Co.

Fig. 262. Battery of crude petroleum stills in a modern refinery.

temperature produces **gas oil**, which is used for the manufacture of illuminating gas. Above 300° **lubricating oil** is obtained. **Petroleum coke** remains in the cylinder. Such a process is known as **fractional distillation**.

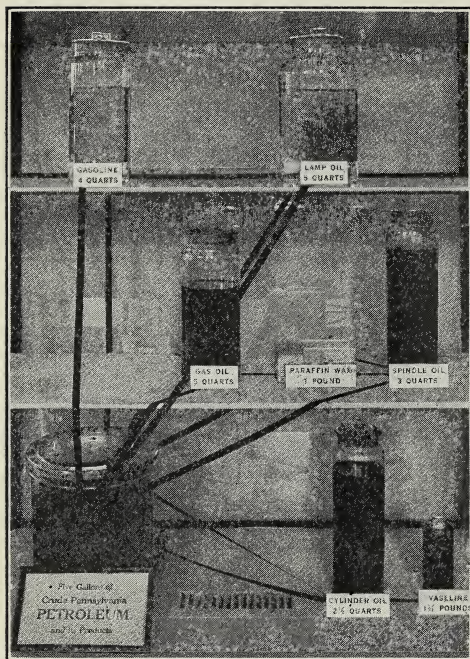
The **naphtha** contains the hydrocarbons from *pentane*, C_5H_{12} , to *nonane*, C_9H_{20} . It is often marketed directly as fuel for motors, or it can be separated by a second distillation into a low-boiling naphtha called **gasoline** and a high-boiling naphtha called **benzine**. The gasoline is suitable for motor spirit, and

the benzine is employed in dry-cleaning and in the manufacture of paint.

The fire hazard in the use of gasoline and benzine is not fully appreciated by the public. No flame or fire should be in the vicinity when these liquids are being handled. Over 1,000 persons are killed and 3,000 severely injured each year in the United States from slight carelessness in this respect.

The kerosene fraction, after additional purification, is marketed as lamp or burning oil.

The lubricating-oil fraction is chilled by brine from an ice machine, whereupon paraffin separates from it in crystalline flakes. The filtered oil is redistilled to separate it into light ("spindle"), medium, and heavy ("cylinder") lubricating oils. Vaseline is one of the products of this second distillation.



Courtesy of the Philadelphia Commercial Museum.

Fig. 263. Products of the distillation of five gallons of crude Pennsylvania petroleum.

This exhibit shows the products in correct amounts. They are: gasoline, 4 qts.; lamp oil, 5 qts.; gas oil, 5 qts.; spindle oil, 3 qts.; cylinder oil, $2\frac{1}{2}$ qts.; paraffin wax, 1 lb.; vaseline, $1\frac{1}{2}$ lb.

COAL TAR

567. Source. Coal tar is a thick, black, foul-smelling liquid which is obtained as a by-product when soft coal is heated for the production of illuminating gas and coke. The following important hydrocarbons are obtained from coal tar by fractional distillation (Fig. 140):

Benzene,¹ C_6H_6 , is a colorless liquid used as motor fuel. When treated with nitric acid, it yields **nitro-benzene**, $C_6H_5NO_2$, which is a faint-yellow oil smelling like bitter almonds. Nitro-benzene when acted upon by nascent hydrogen passes into **aniline**, $C_6H_5NH_2$, a liquid which is the mother-substance of numerous dyes. The vapor of benzene is *poisonous*, and many accidents occur among workmen who enter tanks in which benzene has been stored.

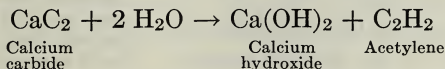
Toluene, C_7H_8 , resembles benzene and like it yields many dyestuffs. It is the mother-substance of **tri-nitro-toluene**, $C_7H_5(NO_2)_3$, the most important of all military explosives.

Naphthalene, $C_{10}H_8$, is sold by druggists under the name of "tar camphor," or "moth balls." It crystallizes in white plates which have a tarry smell. Naphthalene is the raw material of one process for the manufacture of artificial indigo.

Anthracene, $C_{14}H_{10}$, forms colorless, glistening leaflets. It is the mother substance of the important **alizarin** dyes, noted for their fastness toward light and soap, which were formerly obtained from the madder plant.

ACETYLENE, C_2H_2

568. Preparation and properties. The preparation of acetylene from calcium carbide and water has been described (§ 385):



¹The benzene from coal tar must not be confused with the benzine from petroleum.

Apparatus is used in which powdered calcium carbide is gradually fed into water. The acetylene evolved is purified and stored in small gas holders.

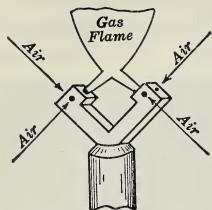
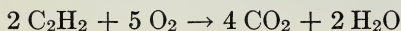


Fig. 264. Acetylene burner.

Acetylene is a colorless gas, which is almost odorless when pure. As ordinarily made, it has an unpleasant odor due to impurities. It can be liquefied by pressure, but no industrial application is made of the liquid for it is a dangerous explosive.

569. Uses. Acetylene is only moderately soluble in water, but it is very soluble in a colorless liquid called **acetone**, which is a product of the distillation of wood. The "Prestolite" cylinders used on automobiles and motor trucks contain asbestos fibre which is saturated with acetone. Acetylene is forced in under pressure and dissolves in the acetone. When the cylinder is used, the pressure is reduced by means of a valve, and the acetylene escapes and burns at the lights of the machine to carbon dioxide and water:



When burned with an ordinary burner, acetylene produces clouds of soot. The burner used with it is shown in Figure 264. Air is drawn in through the side holes on the principle of the Bunsen burner. The two flames strike each other and broaden out into a single clean, colorless flame at right

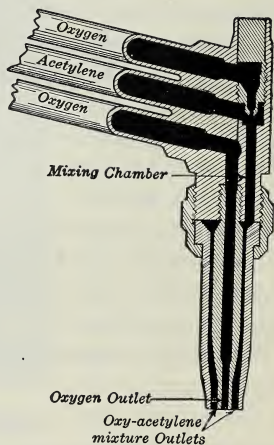


Fig. 265. Oxy-acetylene blow-pipe for metal cutting: six flames of oxy-acetylene mixture heat the metal and it is burned away by the central jet of oxygen.

angles to the plane of the burner. The light resembles sunlight closely and is excellent for judging colors, but acetylene cannot compete with gas and electricity, and it finds a place only in houses in rural districts where gas and electricity are unobtainable.

When acetylene is burned with oxygen in the oxy-hydrogen blowpipe, the flame has a temperature of $3,000^{\circ}$ or more. This oxy-acetylene flame is much used in working metals, in making local repairs, in welding, in cutting girders, etc. In one test with it a circle 20 in. in diameter was cut out of 1-in. steel plate in 45 seconds.

It is an interesting scientific fact that acetylene can be obtained in traces by the direct combination of hydrogen and carbon. This synthesis is carried out by passing hydrogen through a globe in which an electric arc is burning between carbon poles (Fig. 266).

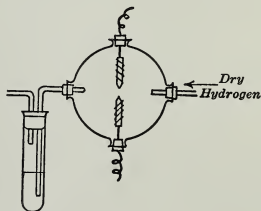


Fig. 266. Synthesis of acetylene.

ASPHALT, TURPENTINE, AND RUBBER

570. Asphalt. Asphalt, or **mineral pitch**, is a hard, black, combustible solid which smells like kerosene. It is composed of a mixture of hydrocarbons. On the island of Trinidad there is a "lake" of asphalt $1\frac{1}{2}$ miles in diameter and of unknown depth. It is cold and hard near the edge, but warm and soft in the center. Deposits of asphalt also occur in California, Texas, and Utah.

In *street paving* a foundation of broken limestone is first put in, and this is covered with a mixture of powdered limestone and asphalt, which is stamped in place with hot irons and then rolled smooth.

The asphalt from Utah, which is quite pure, is known as **gilsonite**. It is used for making asphalt varnish or "**japan**,"



Photographs by Charles R. Toothaker.

Fig. 267. The asphalt lake in Trinidad.

The escape of bubbles of inflammable gas through the surface water shows that the hard asphalt has lost the volatile constituents of the original mass.

which is prepared by dissolving gilsonite in turpentine. Such varnish is used for protective coatings to be baked on steel in the manufacture of automobile bodies, bicycles, gas ranges, etc.

571. Turpentine, $C_{10}H_{16}$. If a portion of the bark of a pine tree be removed and the trunk scarified, sap oozes from the wounded portion and can be collected in a suitable vessel. When this sap is distilled, **turpentine** vaporizes, and **rosin** remains in the retort.

Turpentine is a thin, colorless liquid with an agreeable odor. It is lighter than water and insoluble in it. Turpentine is largely used in making paint and varnish.

Rosin is a brittle, brown, transparent solid which contains carbon, hydrogen, and oxygen, but of which the formula is still somewhat uncertain. It is used in sizing paper, in preparing lubricants, in making cheap soaps, as a constituent of varnish, and in filling shrapnel shells. One method of making *lamp-black* is by burning rosin with an insufficient supply of air.

572. Rubber, $C_{10}H_{16}$.

Rubber has been made artificially, but not cheaply enough to compete with the natural product. The rubber of commerce is obtained from a tree which grows wild in Brazil, Central Africa, and in other tropical regions and is now largely cultivated in Ceylon, the Malay Peninsula, and the East Indies. The tree is tapped by making an incision in the bark (Fig. 268), from which a milky juice called *latex* exudes and is collected in a tin cup. Formerly all our crude rubber came from wild trees, principally from Brazilian jungles. The collectors prepared it for transportation by dipping wooden



Courtesy of W. R. Grace & Co.

Fig. 268. Tapping for rubber in Ceylon closely resembles tapping for turpentine in Florida.

paddles in the latex and exposing them to the smoke of burning wood, which coagulated the liquid in a thin film. This process was repeated again and again until large lumps of rubber were built up which reached the market in dark masses about the size of large watermelons. At present more than 80 per cent of the world's rubber production comes from cultivated plantations, the product of which is superior to wild rubber in uni-



Courtesy of the Goodyear Tire & Rubber Co.

Fig. 269. Inspecting and packing "crepe" rubber on a Sumatra plantation.

formity, cleanliness, and cheapness. On the plantations the latex is strained and then coagulated by the addition of a weak solution of acetic acid. The rubber which separates is run through machines which send it to the market in long, thin, narrow sheets of "crepe" rubber.

Crude rubber is hard and inelastic, and it is always **vulcanized** before use. The crude rubber is passed many times between grooved rolls, which tear it to pieces. At the same time it is sprayed with water to wash out dirt. After thorough

drying in a vacuum dryer the rubber goes to the mixing rolls, where it is incorporated with the proper amount of sulphur for vulcanization (7 per cent for soft-rubber goods and 30 per cent for hard rubber or *ebonite*) and with the "*fillers*." These fillers consist of various powdered substances added to reduce cost and to give the product wearing qualities.

Zinc oxide is largely used for this purpose in white rubber, and lead oxide in black. In red rubber mercuric sulphide, antimony sulphide, or ferric oxide is employed. Many of the fillers mentioned above are poisonous and should not be used if the rubber is intended for children's toys. More or less "*reclaimed rubber*," extracted from old rubber shoes, tires, etc., is added with the fillers, though this has a bad effect on the quality of the finished product.

The material is rolled into sheets of suitable thickness and is then ready to be *moulded*. The vulcanization of the finished article is effected by heating it with steam to 150°. During this heating the rubber combines chemically with sulphur, and the characteristic tenacity and elasticity are developed.

It will be noticed that the formula of rubber is the same as that of oil of turpentine. However, the molecular weight of

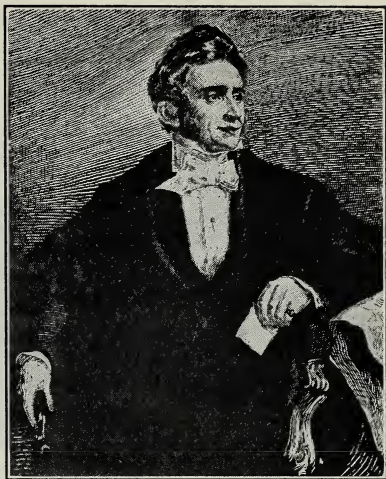


FIG. 270. CHARLES GOODYEAR
(1800-1860).

American inventor; discovered the process of vulcanization which fits rubber for its manifold uses by destroying its adhesiveness and preserving its elasticity under all conditions of temperature.

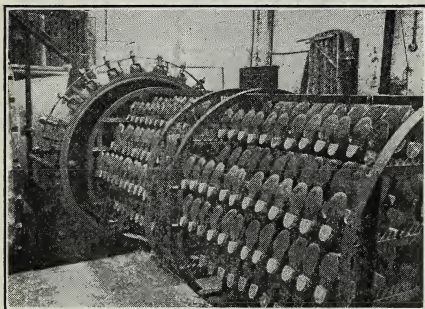
rubber is unknown, and its real formula is probably some multiple of $C_{10}H_{16}$.

SUBSTITUTION PRODUCTS OF THE HYDROCARBONS

573. When chlorine acts upon methane, chlorine atoms are *substituted* one by one for the hydrogen atoms, producing first CH_3Cl and finally CCl_4 .

Three of these **chlorine substitution products** are the following:

Methyl chloride, CH_3Cl , is a gas easily compressed to a liquid, which is sold in small metal cylinders to dentists. When the liquid is sprayed upon the gum, it produces a local temporary freezing, which makes it



Copyright, Publishers' Photo Service.

Fig. 271. Charging a vulcanizer with rubber shoes.

possible to extract teeth without pain.

Chloroform, $CHCl_3$, is made by distilling alcohol or acetone with bleaching powder. It is a dense, colorless liquid with an agreeable odor. Chloroform is an important anæsthetic.

Carbon tetrachloride, CCl_4 , is a heavy, colorless liquid, which, on account of the quenching effect of its vapor upon flame, is used in one type of fire extinguisher. Carbon tetrachloride is the chief constituent of "**carbona**," which is used in the household for removing grease spots.

The hydrogen atoms of other hydrocarbons can be replaced in a similar way by chlorine and other elements and also by radicals, so that the total number of substitution products is very great.

SUMMARY

Petroleum is a mixture of hydrocarbons, which in Pennsylvania petroleum belong to the **methane series**, of which the general formula is C_nH_{2n+2} .

The **refining** of petroleum is a process of fractional distillation by which the crude oil is separated into **naphtha**, **kerosene**, and **lubricating oil**.

Coal tar when distilled yields hydrocarbons, of which the most important are **benzene**, C_6H_6 , **toluene**, C_7H_8 , **naphthalene**, $C_{10}H_8$, and **anthracene**, $C_{14}H_{10}$.

Turpentine, $C_{10}H_{16}$, is obtained by distilling the sap of the pine. **Rosin** remains in the retort.

Asphalt is a complex mixture of hydrocarbons.

Crude **rubber**, $C_{10}H_{16}$, is the thickened sap of a tropical tree. In **vulcanizing** the rubber combines chemically with sulphur.

Chlorine and many other elements can be substituted atom for atom for the hydrogen in methane and other hydrocarbons.

EXERCISES

1. Explain the fact that rubber and turpentine have the same formula, although their properties are so different.
2. Calculate the percentages of carbon and hydrogen in the first five members of the methane series.
3. How is petroleum *refined* for use?
4. What is *coal tar*? What are the most important products obtained from it?
5. Distinguish between benzine and benzene.
6. What is *asphalt*? Discuss two uses of asphalt.
7. How is turpentine obtained? Rosin? What are the chief uses of both?
8. How is crude rubber obtained?
9. What is meant by *vulcanization*? What "fillers" are used in rubber?

10. What substitution products are formed by the regulated action of chlorine upon methane?

11. What precautions would you take in removing grease spots from clothing in the kitchen of the home by means of gasoline? What is the advantage of carbon tetrachloride over gasoline?

12. The use of cylinders containing liquid acetylene for illumination is forbidden, while that of Prestolite cylinders is permitted. Why?

13. A handful of rubber bands was carelessly thrown on a silver plate standing on the sideboard. The plate rapidly became badly tarnished. Explain.

14. Why was rubber of small importance until Goodyear discovered the vulcanizing process?

15. What is meant by the statement that carbon tetrachloride is a *substitution product* of methane?

16. Hundreds of hydrocarbons are known. What would you say about the total number of substitution products?

17. The radical NO_2 is called the *nitro* group. Explain the name and formula of the most important military explosive. Is it a substitution product? What is its exact relation to the hydrocarbon from which it is made?

CHAPTER XLI

THE CARBOHYDRATES

574. Definition. A carbohydrate is a compound which contains *carbon* combined with hydrogen and oxygen in the proportions in which these two elements exist in water, H_2O , that is, 2 *atoms* of hydrogen to 1 *atom* of oxygen, or 1 part of hydrogen to 8 parts of oxygen by weight. Ordinary sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is the most familiar carbohydrate. Carbohydrates occur in animals, but they are chiefly obtained from plants. They form important constituents of many food products. A list of some of the more important carbohydrates follows:

IMPORTANT CARBOHYDRATES

Familiar Name	Scientific Name	Formula	Appearance	Source
STARCH	Starch	$\text{C}_6\text{H}_{10}\text{O}_5$	White powder	Corn, potatoes
PLANT FIBRE	Cellulose	$\text{C}_6\text{H}_{10}\text{O}_5$	White fibres	Cotton, flax, wood, hemp, jute, ramie, etc.
GRAPE SUGAR	Dextrose	$\text{C}_6\text{H}_{12}\text{O}_6$	Colorless crystals	Starch
FRUIT SUGAR	Levulose	$\text{C}_6\text{H}_{12}\text{O}_6$	"	Sucrose
SUGAR	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	"	Cane, beet
MILK SUGAR	Lactose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	"	Milk

It will be noted that the last two substances in the above table, cane sugar and milk sugar, possess the *same formula*, although their properties are quite different, milk sugar being

less sweet, less soluble in water, and more easily digested than cane sugar. The explanation is that although the molecules of the two carbohydrates contain the *same atoms*, yet these atoms are *differently arranged* in the two cases. The same group of chessmen can be set up upon the board to present an infinite variety of situations in the game, and it is the same with the atoms in the molecule. The same explanation holds good for starch and cellulose and for dextrose and levulose; in fact, such cases are common among the carbon compounds.

STARCH, $C_6H_{10}O_5$

575. Occurrence. Starch is abundant in plants, being found especially in the cereals, such as corn, wheat, rice, and barley, and in tubers like potato and cassava. Wheat flour contains three-quarters of its weight of starch.

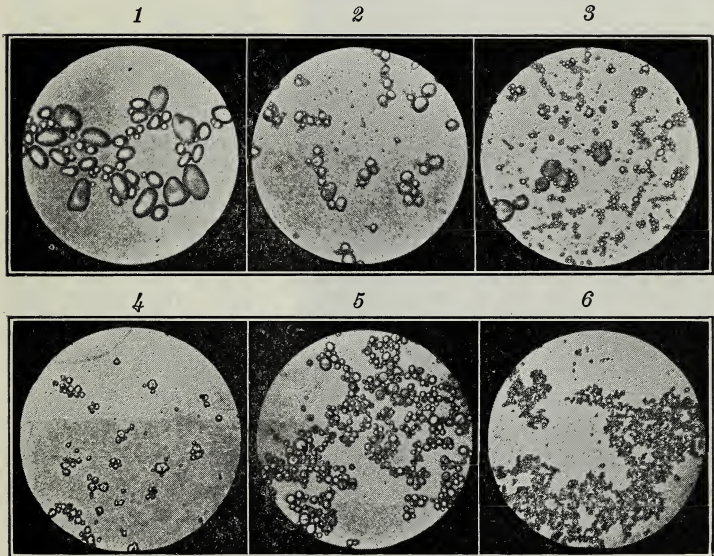
Starch occurs in microscopic *granules*, which differ in size and shape in different plants. The largest starch granules, those of the potato, are $\frac{1}{300}$ in. in diameter, while the smallest, the rice starch granules, have a diameter of only $\frac{1}{3000}$ in. The source of any sample of starch can easily be determined, therefore, by examination with the microscope. A single grain of wheat, which would weigh about 0.4 gram, contains from 10 to 20 million starch granules.

576. Extraction. In the United States starch is obtained chiefly from corn, which contains 60 per cent of starch. The corn is softened by soaking it in water containing a little sulphur dioxide and is then crushed. The pulp is placed upon fine silk bolting cloth and shaken under a spray of water. The plant fibre is detained, while the starch and the **gluten**, which is the *protein* of the grain, pass through. The milky liquid is allowed to flow down tables 4 ft. wide and 120 ft. long, with a slope of only 4 in. in the whole length. Here the starch deposits. It is finally removed and dried for 20 hours at 80°.

The liquid that flows off the tables, which still contains the

gluten, is forced through cloth filters. The cake of gluten formed is dried, ground, and sold as "gluten meal" for cattle food.

Potatoes are soaked and washed and then cut to pulp by machines containing revolving cylinders set with knives. The starch is then extracted as described above.



Courtesy of The A. E. Staley Manufacturing Co.

Fig. 272. Photomicrographs of starch granules from different sources, enlarged 75 diameters: 1, potato; 2, wheat; 3, rye; 4, corn; 5, tapioca; 6, rice.

Wheat starch is made by kneading dough made from wheat flour in machines equipped with grooved rolls. The starch is washed through sieves by jets of water and treated as in the manufacture of corn starch.

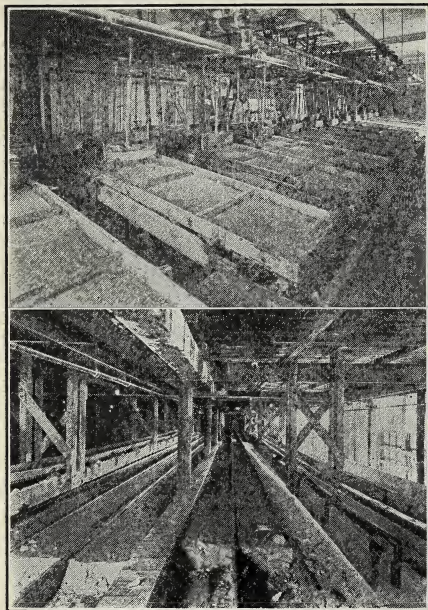
Tapioca is a form of starch extracted from the cassava, a tuber cultivated in the tropics. Since the cassava often con-

tains considerable quantities of *hydrocyanic acid*, HCN, tapioca is washed carefully to remove this dangerous poison.

577. Properties and uses. Starch is a white powder, which is insoluble in cold water. When heated with water it forms

a *colloidal* solution (§ 82), which is pasty if it contains a high percentage of starch. A solution containing free iodine, when mixed with starch paste, produces a deep blue color, and this forms a delicate *test* for starch.

The largest use of starch is in laundry work, for which rice starch is best, though corn starch and wheat starch are largely in use. Rice starch is used for toilet powder. Wheat starch is the best for making paste. Starch is also used for thickening colors in calico printing and as a food, as, for instance,

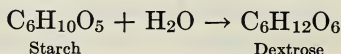


Courtesy of the A. E. Staley Manufacturing Co.

Fig. 273. Starch shakers (above) and settling tables (below).

in corn starch, arrow-root starch, and tapioca.

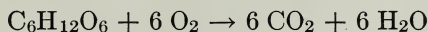
During digestion each molecule of starch combines with a molecule of water and passes into a sugar called **dextrose**, $C_6H_{12}O_6$, which is soluble in water and is absorbed into the blood:



A large part of the food value of tubers, cereals, and many other vegetable food products is due to the fact that they contain a high percentage of starch.

578. Dextrin, $C_6H_{10}O_5$. The raw material for making dextrin is *sago starch*, a product of the sago palm which is imported from the Far East. To convert it into dextrin, the sago starch is heated in revolving steam-heated cylinders to 250° , and the product ground and sieved through bolting cloth. Dextrin is a pale-yellow powder, which, unlike starch, dissolves in cold water, forming a liquid possessing strong adhesive properties. It is used as an adhesive on postage stamps and envelopes, in making mucilage, and in thickening colors for calico printing.

579. Glycogen, $C_6H_{10}O_5$. Glycogen, often called **animal starch**, is a white powder similar to starch but not identical with it. After a meal rich in carbohydrates, glycogen is stored up in the liver, which may contain 5 oz. or more of it. Like starch, glycogen easily takes up a molecule of water and is converted into **dextrose**, $C_6H_{12}O_6$, which during muscular work is carried from the liver to the muscular cells and there oxidized to carbon dioxide to furnish energy:



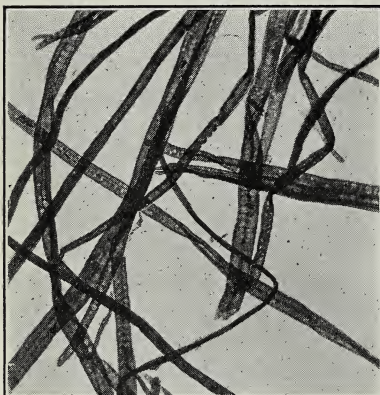
CELLULOSE, $C_6H_{10}O_5$

580. Occurrence. Cellulose occurs only in plants. It forms the envelope of the plant cell, the container in which the chemical processes take place, just as the chemical processes of the laboratory are carried out in glass. Wood, straw, cotton, linen, and paper are chiefly composed of cellulose. Filter paper of the best quality is practically pure cellulose.

581. Properties. Cellulose is a white, combustible solid which has never been obtained in crystals. It is insoluble in most liquids. It is obtained by treating plant products rich

in cellulose with solutions that dissolve and remove the other constituents, so that the cellulose is obtained as a residue.

582. Paper. Wood consists of a mass of fibres of cellulose, held together by a cement termed **lignose**. In the manufacture of **paper** the wood is cut into chips and heated under pressure in a strong boiler with a solution of sodium hydroxide or of cal-



Courtesy of J. M. Finch.

Fig. 274. Cellulose fibres from wood pulp, enlarged 50 diameters.

cium hydrogen sulphite, $\text{Ca}(\text{HSO}_3)_2$. The liquid dissolves the lignose and yields a **pulp** composed of cellulose fibres, which is then bleached by treatment with bleaching powder. After washing and draining, the pulp passes into the "hollander," a vat in which a horizontal roll set with knives rotates close to stationary knives set in a metal bed plate.

Here the pulp is thoroughly disintegrated, and the "*filler*," a white powder

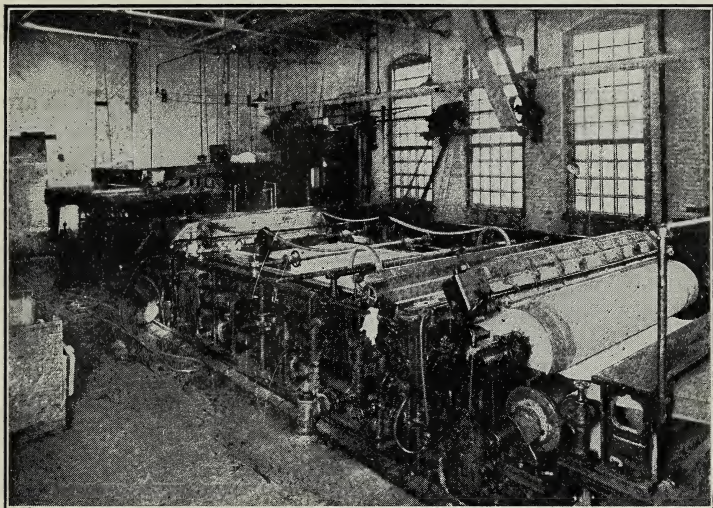
composed of clay or barium sulphate, and the *size*, a cement composed of rosin, sodium hydroxide, and aluminum sulphate, are added.

The pulp now flows on an endless belt of wire gauze which forms part of the paper machine. The water partly drains off through the gauze, and it is completely removed when the paper passes between heavy iron rolls which are heated by steam. The paper then passes under heavy pressure through polished cast-iron rolls, called "*calenders*," which give a smooth finish to the surface.

The cheapest grade of wrapping paper is made by grinding wood, mixing the pulp with size, and putting it through the

paper machine without bleaching or chemical treatment of any kind. The finer qualities of writing paper are made from linen rags, which are sorted, cleaned, and bleached. They are then disintegrated and mixed with size and filler in the hollander, and the pulp introduced into the paper machine.

583. Artificial silk. Artificial silk is made from cellulose in the form of pure chemical wood pulp. The pulp is placed in



Courtesy of the American Writing Paper Co.

Fig. 275. The wet end of a paper machine, showing the pulp flowing out on the endless belt of wire gauze and the first compression rolls.

wire baskets and soaked in a solution of sodium hydroxide. It is then put into a mixing machine with 30 per cent of carbon disulphide, CS_2 , and after thorough mixing pure water is added, whereupon a yellow solution called **viscose** is formed. This liquid is squirted through an orifice 0.1 mm. in diameter into a solution of *ammonium sulphate*, $(\text{NH}_4)_2\text{SO}_4$, where it coagulates to form a filament of cellulose, which, when spun, woven, and dyed, is **artificial silk**.

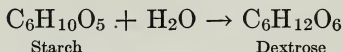
It will be seen that artificial silk is merely a lustrous form of cellulose and is quite different from natural silk, which is composed of a protein secreted by the silkworm. When wet, artificial silk loses four-fifths of its tenacity, so that great care is required in handling it in the dye vat.

The thin transparent film used to cover confectionery and to form a part of certain envelopes is made by the viscose process.

THE SUGARS

The **sugars** are a numerous class of carbohydrates which are freely soluble in water and have a sweet taste. The most important sugars correspond either to the formula $C_6H_{12}O_6$ or to the formula $C_{12}H_{22}O_{11}$.

584. Dextrose, $C_6H_{12}O_6$. Dextrose, or **grape sugar**, is abundant in grapes and many other fruits and makes up one-third of honey by weight. It is made by heating corn starch with very dilute hydrochloric acid in an airtight copper vessel under a pressure of 50 lb. to the square inch. The acid is a catalyst, the chemical change occurring between the starch and the water:



After 15 minutes the conversion of the starch into dextrose and dextrin is complete. The hydrochloric acid is then neutralized with sodium carbonate, and the liquid decolorized by filtration through a thick layer of boneblack and evaporated in vacuum vessels to a sirup which contains half its weight of dextrose and 30 per cent of dextrin, the balance being water.

Pure dextrose, which resembles ordinary sugar but is less sweet, can be obtained from this sirup, but this is rarely done. As a rule the sirup is marketed directly, under the name **glucose**, to the manufacturer of jellies, jams, and candy and as a table sirup.

Cellulose, like starch, can be changed into dextrose by treatment with dilute acid, but the conversion is more difficult and is just beginning to receive industrial application.

Levulose, $C_6H_{12}O_6$, often called **fruit sugar**, is abundant in ripe fruits and in honey. It is a white, crystalline solid much sweeter than dextrose. It is used in the manufacture of jellies, jams, and marmalades and in foods for persons suffering from diabetes.

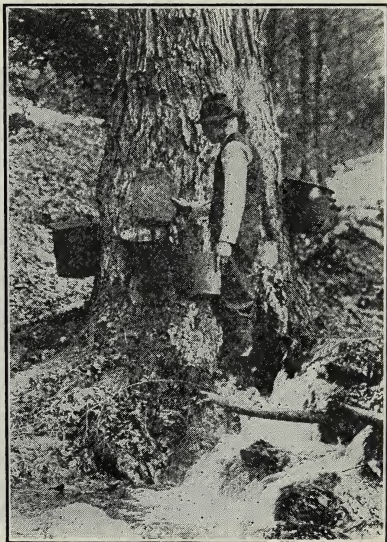
585. Sucrose, $C_{12}H_{22}O_{11}$.

Sucrose is the familiar **sugar** of the household. It is widely distributed in our vegetables and fruits. Onions, carrots, peaches, and apples each contain about 6 per cent of it, and it is found in corn and barley, in sorghum, in honey, and in the sap of sycamore, birch, and maple trees.

Maple sugar is obtained by making an incision into the trunk of the sugar-maple tree, collecting the sap, and boiling it down over an open fire. It contains impurities which give it a peculiar, agreeable flavor. The pure sugar of commerce is derived from the **sugar cane** and the **sugar beet**.

The sugar cane is a species of tropical grass which reaches a height of from 6 to 20 ft. and which contains as much as 20 per cent of sugar. The leading producers of cane sugar are Cuba and Hawaii.

In the tropics the cane is passed between heavy iron rolls,

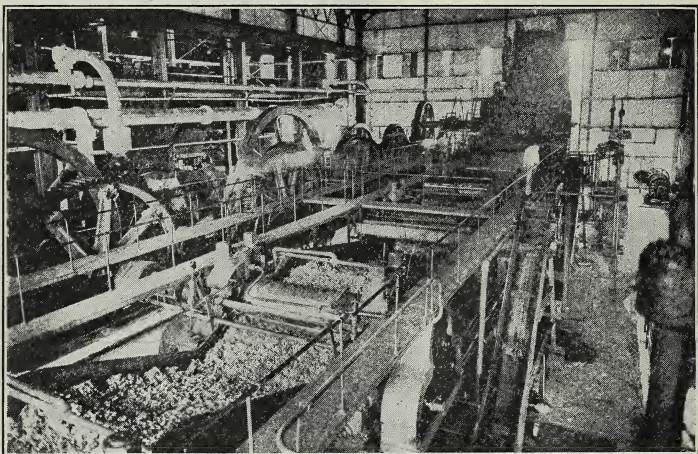


Courtesy of the "Scientific American."

Fig. 276. Collecting sap from the sugar maple.

which squeeze out the juice, and this is boiled down to obtain "raw sugar" for export. The liquid remaining after the sugar has separated is a kind of **molasses**, often called "**black strap**." It is exported and used for the manufacture of industrial alcohol, of which it is the chief source.

In the refineries of the United States and Europe the brown impure sugar is dissolved in warm water and the solution



Courtesy of the "Scientific American."

Fig. 277. Cane crushing rolls in a Cuban sugar mill.

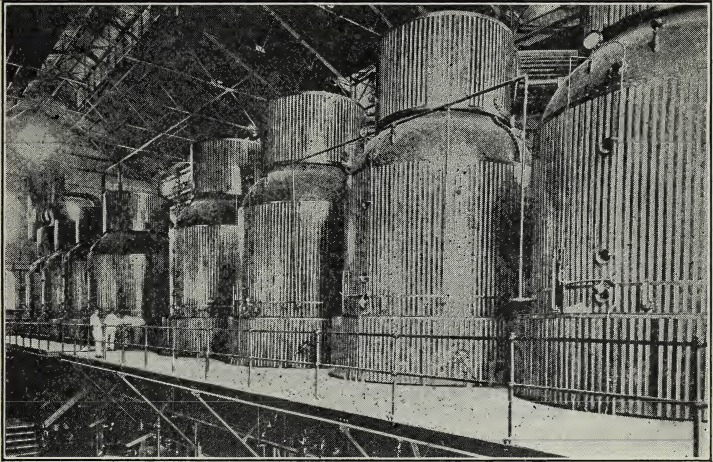
filtered through bags of thick canvas to remove dust and plant fibre. The clear, brown liquid then passes slowly through a thick layer of boneblack, which removes the coloring matter (§ 265).

The colorless sirup is boiled down in a vacuum vessel until crystals of sugar separate. The moist crystals are partially dried in a perforated centrifugal machine, and the drying is completed in a large steam-heated cylinder, which is kept in motion to prevent the crystals from sticking together. After

the addition of a trace of ultramarine to correct a slight yellow tint, the product is sold as "**granulated sugar.**"

Pulverized sugar is made by powdering the granulated. Cube sugar and "domino" sugar are prepared by moistening granulated sugar with sugar solution, forming the moist mass into the desired shape, and drying.

The sugar beet thrives in temperate regions with abundant



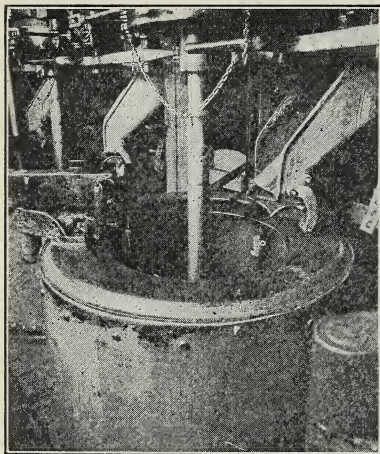
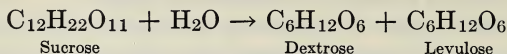
Courtesy of the "Scientific American."

Fig. 278. A battery of vacuum pans.

sunlight. Selected specimens have contained 27 per cent of sucrose. The average is 16 per cent. Extraction is begun by cutting the beet into thin slices, which are treated with warm water to dissolve the sucrose. The refining is similar to that of cane sugar, and the final product is identical.

Sucrose crystallizes in colorless prisms which are seen in pure condition in "**rock candy.**" It is very soluble in water. When the solution is boiled with a trace of hydrochloric acid, each molecule of sucrose takes up a molecule of water

and separates into a molecule of dextrose and one of levulose:



Copyright, Ewing Galloway.

Fig. 279. Centrifuge for drying sugar crystals.

Levulose is prepared industrially in this way.

586. Lactose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

Lactose, or **milk sugar**, is contained to the extent of 5 per cent in cows' milk and is obtained as a by-product of the manufacture of cheese. Lactose is a white crystalline substance, not so sweet as sucrose and less soluble in water. It is used as a constituent of foods for infants and invalids and as a cementing material in medicinal tablets.

SUMMARY

A carbohydrate contains carbon united with hydrogen and oxygen in the proportion of 2 atoms of the first to 1 of the second.

Starch, $\text{C}_6\text{H}_{10}\text{O}_5$, is obtained from corn and other grains and from potatoes.

Cellulose, $\text{C}_6\text{H}_{10}\text{O}_5$, is the chief constituent of wood, paper, cotton, linen, and artificial silk.

Dextrose, $\text{C}_6\text{H}_{12}\text{O}_6$, is obtained in a solution known as **glucose**, or **corn sirup**, by heating starch under pressure with 1-per cent hydrochloric acid.

Levulose, $\text{C}_6\text{H}_{12}\text{O}_6$, resembles dextrose but is much sweeter.

Glycogen, $C_6H_{10}O_5$, is stored up in the liver and is drawn upon during muscular work.

Sucrose, or common sugar, $C_{12}H_{22}O_{11}$, is obtained from the sugar cane and the sugar beet.

Lactose, $C_{12}H_{22}O_{11}$, is the sugar of milk.

EXERCISES

1. Explain the distinction between a *hydrocarbon* and a *carbohydrate*.
2. Calculate the percentage composition of sucrose.
3. How many grams of dextrose and how many of levulose are formed when 171 grams of sucrose are boiled with dilute hydrochloric acid?
4. In what way can the source of a sample of starch be ascertained?
5. How is starch extracted from corn, potatoes, and wheat?
6. Describe glycogen, and explain its function in the body.
7. How is paper manufactured from wood?
8. Describe the production of artificial silk.
9. Explain the preparation of glucose sirup.
10. Describe the extraction of raw sugar from the cane and the conversion of the raw sugar into refined sugar.
11. How is it possible for two carbohydrates to have the same formula, although the two differ greatly in properties? Give three instances.
12. Make a tabular comparison of the hydrocarbons and the carbohydrates, including sources, properties, uses, and behavior in the body.
13. Which would give the larger number of calories when oxidized, a pound of sugar or an equal weight of gasoline? Why?
14. In drying starch great care is taken to avoid overheating. Why?
15. There is a widespread popular prejudice against the use of glucose in food products. Is there any real objection to the moderate use of glucose at the table? Why?

16. Bread contains dextrin. In what portion of the loaf would you look for it?

REVIEW QUESTIONS

1. The molecular weights of sucrose, dextrose, and levulose have been accurately determined, but we are ignorant of the molecular weights of cellulose and starch. Why?

2. Mercuric oxide can neither be vaporized nor dissolved as such. Do we know its molecular weight? Why? What is meant, then, by the formula HgO ?

3. How would you determine the molecular weight of hydrogen chloride? Of sucrose?

4. Enumerate three substances, other than those referred to in the foregoing questions, of which the molecular weights cannot be determined at present.

5. Students often claim that the molecular weight of cellulose can be determined by adding the weights of the atoms in the formula $\text{C}_6\text{H}_{10}\text{O}_5$, which gives a result of 162. Criticize this statement.

CHAPTER XLII

ALCOHOLS, ACIDS, AND ESTERS

ALCOHOLS

587. General. Corresponding to each of the hydrocarbons of the methane series is a compound called an **alcohol**, in which a hydrogen atom of the hydrocarbon is replaced by the radical **hydroxyl**, OH:

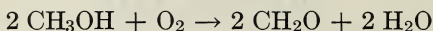
Hydrocarbon	Alcohol
Methane, CH_4	Methyl alcohol, CH_3OH
Ethane, C_2H_6	Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$
Propane, C_3H_8	Propyl alcohol, $\text{C}_3\text{H}_7\text{OH}$
<i>etc.</i>	<i>etc.</i>

It will be noted that the term alcohol is not the name of a single substance, but of a *class* of compounds. There are hundreds of alcohols. The simpler alcohols are transparent liquids with a spirituous odor, but the higher members of the series are colorless waxy solids. Only three alcohols, which are of great practical importance, can be described here. These are **methyl alcohol**, **ethyl (ordinary) alcohol**, and **glycerine**.

588. Methyl alcohol, CH_3OH . Methyl alcohol is commonly called **wood alcohol** because it is obtained by the distillation of wood (§ 263). It is a colorless liquid resembling ordinary (ethyl) alcohol, but its odor, though similar, is not identical, and it boils at a lower temperature (65°). Methyl alcohol is used in making varnish, in the manufacture of dyes, in **denaturing** ordinary alcohol, and in making **formaldehyde**.

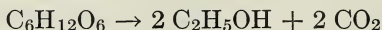
Methyl alcohol is intensely *poisonous*. It affects the optic nerve, and when the quantity taken is too small to kill, it often produces total blindness.

589. Formaldehyde, CH_2O . Formaldehyde is made by leading the vapor of methyl alcohol, mixed with air, over heated copper wire:



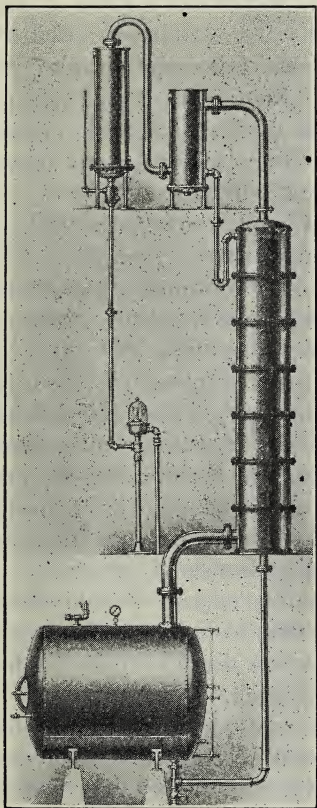
Formaldehyde is a colorless gas with a penetrating odor. Its 40-per cent solution in water is sold under the name **formalin**. Formaldehyde is an excellent disinfectant, and it does not tarnish metal objects or bleach colored fabrics. It is largely used for fumigating rooms, clothing, furniture, etc.

590. Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$. The most important source of **ethyl**, or ordinary, **alcohol** is the "black strap" molasses obtained as a by-product of the extraction of crude cane sugar in Cuba, Hawaii, and elsewhere. This is a dark, sirupy liquid which contains dextrose and levulose. It is diluted with water in large vats and **yeast** added, whereupon both the dextrose and the levulose **ferment**, passing into alcohol and carbon dioxide:



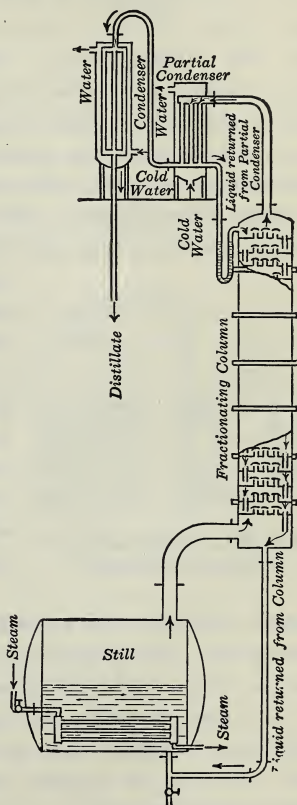
The carbon dioxide escapes in bubbles, while the alcohol remains dissolved in the water present, from which it is afterwards separated by **fractional distillation**. The boiling point of alcohol ($78^\circ.5$) is much lower than that of water. Hence, when a mixture containing both alcohol and water is boiled, the vapor that escapes is much richer in alcohol than is the liquid that remains behind. The stills which are used on a large scale are based on this fact, and by means of them it is possible to obtain 95-per cent alcohol from the product of fermentation in a single distillation. A simple type of industrial still is shown in Figure 280. Water vapor is condensed in the fractionating column and partial condenser and returned to the still. The more volatile alcohol is not condensed until it reaches the condenser.

Alcohol is also made from vegetable products rich in starch, especially from corn in the United States and from potatoes in Europe. The corn or potatoes are steamed, crushed, and

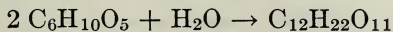


Courtesy of the Walter F. Lummus Co.

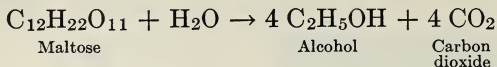
Fig. 280. Commercial alcohol still and fractionating column.



warmed gently with a solution of **malt**, which converts the starch into a sugar called **maltose**, $C_{12}H_{22}O_{11}$:



The liquid is then cooled and yeast added, whereupon the maltose ferments:



As with "black strap," the alcohol is separated from the aqueous liquid by fractional distillation. The liquid remaining in the still is used as food for cattle. The malt for the process is obtained by moistening barley, allowing it to sprout, and killing the young plant by a gentle heat.

591. Fermentation. The fact that dextrose ferments with yeast can be shown with the apparatus of Figure 281. The large bottle contains 100 grams of dextrose, or 200 grams of sirup, dissolved in a liter of water. A yeast cake, crushed in a little water, has been added. The small bottle contains limewater, to serve as a test for carbon dioxide, and the U-tube is filled with fragments of sodium hydroxide to keep out the carbon dioxide of the air.

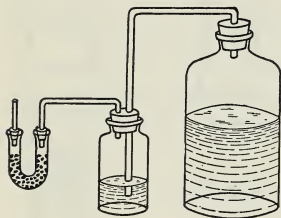


Fig. 281. Fermentation of dextrose with yeast.

Bubbles appear in the large bottle, while the white precipitate that forms in the limewater shows that the escaping gas is carbon dioxide. The alcohol can be obtained by fractional distillation.

Levulose ferments in the same way, the equation being identical. Sucrose does not ferment *directly*, but the yeast first converts the sucrose into dextrose and levulose, both of which then ferment.

592. Properties of alcohol. Ethyl alcohol is a colorless liquid with a pleasant odor and a burning taste. Its specific gravity is 0.8. It freezes at -130° to a white mass. Alcohol mixes with water in all proportions, not forming two layers. The percentage of alcohol in such a mixture can be determined

at once by taking the specific gravity with a hydrometer and referring to tables which have been calculated for the purpose.

Alcohol takes fire readily and burns with a blue flame to carbon dioxide and water. When pure alcohol is taken into the body, it extracts water energetically from the tissues and acts as a violent poison.

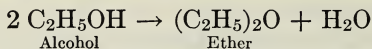
593. Industrial alcohol. Alcohol is used as a solvent of shellac and other resins in making varnish; in making transparent soaps, collodion, celluloid, and smokeless powder; in the preparation of important drugs, like chloral, chloroform, iodoform, and ether; in making perfumery; and by the druggist in preparing his "spirits," "tinctures," and "extracts," all of which are alcoholic solutions.

Alcohol intended for the industries is often **denatured**, that is, mixed with substances that give it a disgusting odor and taste and make it unfit for use as a beverage. Such alcohol is tax-free, whereas the tax on each gallon of pure alcohol amounts to many times the cost of production. Alcohol can be denatured by adding 10 per cent of crude wood alcohol and 0.5 per cent of benzine, or by the addition of 2 per cent of wood alcohol and 0.5 per cent of bone oil. *On account of the methyl alcohol it contains, denatured alcohol is poisonous. It must not be employed in the preparation of anything that is to be taken internally, nor should it be used for bathing the body.* Another denaturing formula which is now in extensive use consists in mixing the alcohol with 2.5 per cent of benzene, 0.5 per cent of nitrobenzene, and 0.2 per cent of pine oil. The product is less poisonous than alcohol denatured by wood alcohol but is still entirely unfit for internal use.

The blue flame of alcohol deposits no soot, and it forms an excellent fuel for spirit lamps and chafing dishes. For convenience the alcohol is often sold in a **solid** form obtained by dissolving soap in 90 per cent alcohol. As a motor fuel alcohol forms a good substitute for gasoline. Alcohol is safer to store and to handle, but it is more expensive than gasoline at pres-

ent. However, the price of gasoline is likely to rise, whereas that of alcohol will ultimately fall.

594. Ethyl oxide, $(C_2H_5)_2O$. Ethyl oxide, commonly called **ether**, is made by heating alcohol with sulphuric acid, which removes the elements of water from two molecules of alcohol:



Ether is a colorless, combustible liquid, which boils at 35° and vaporizes so rapidly that a sensation of intense cold is noticed when it is placed upon the skin. Ether is the leading anæsthetic. It is also employed by florists for forcing plants. Lilacs or azaleas, exposed for 24 hours to air containing ether, bloom 7 to 10 days earlier than without this treatment.

595. Glycerine, $C_3H_5(OH)_3$. Glycerine is an alcohol derived from *propane*, C_3H_8 , by the replacement of 3 hydrogen atoms by 3 hydroxyl radicals. It is an important constituent of fats and oils and is obtained from them as a by-product of the soap industry and of the candle industry.

Glycerine is a thick, colorless liquid with a sweet taste, which boils at 290° , freezes at -40° , and does not evaporate at ordinary temperatures. For this reason it is useful when an object is to be kept moist, as in the ink pads for rubber stamps. It is a frequent constituent of the toilet preparations prepared by the pharmacist. Its chief use is in the manufacture of **nitroglycerine** and **dynamite** (§ 605).

THE ACIDS

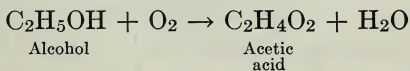
Corresponding to each hydrocarbon of the methane series is an **acid** of the general formula $C_nH_{2n}O_2$:

Hydrocarbon	Acid
Methane, CH_4	Formic acid, CH_2O_2
Ethane, C_2H_6	Acetic acid, $C_2H_4O_2$
* * *	* * *
Hexadecane, $C_{16}H_{34}$	Palmitic acid, $C_{16}H_{32}O_2$
Octadecane, $C_{18}H_{38}$	Stearic acid, $C_{18}H_{36}O_2$

Only one of the hydrogen atoms in the molecules of these acids can be replaced by metals.

596. Acetic acid, $C_2H_4O_2$. Acetic acid is obtained as a by-product of the distillation of wood. It is a colorless, acid liquid, which blisters the skin if allowed to remain upon it. Acetic acid is used in pharmacy, in making artificial flavors, in dyeing wool and silk, in the manufacture of white lead, in making dyestuffs, and in preparing useful acetates. The acetates of aluminum, chromium, and iron are valuable mordants, and lead acetate is employed in pharmacy.

597. Vinegar. Vinegar is a solution containing 4 to 10 per cent of acetic acid with impurities and flavoring substances depending upon the method by which it is made. When cider remains exposed to air, vinegar is produced because the alcohol of the cider is slowly oxidized to acetic acid:



The oxidation is brought about by living organisms called **acetic-acid bacteria**, which are found in countless numbers in the liquid. The same change takes place in wine, or in any dilute alcoholic solution, when infected with acetic-acid bacteria and exposed to air.

In the *quick vinegar process* a cask with a perforated bottom is packed with beechwood shavings which are moistened with vinegar to infect them. The dilute alcoholic liquid is allowed to drip slowly through the cask and, on account of the large surface exposed to the air, is rapidly transformed to vinegar.

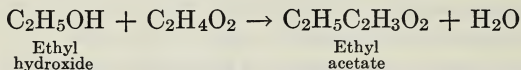
598. Palmitic acid, $C_{16}H_{32}O_2$, and stearic acid, $C_{18}H_{36}O_2$, are colorless, waxy solids which feel greasy to the touch. They are important constituents of the animal and vegetable fats and oils. Both acids find extensive application in the candle industry and in the soap industry.

Oleic acid, $C_{18}H_{34}O_2$, belongs to a different series of acids. It is contained abundantly in oils like olive oil, cottonseed oil,

and the like. Pure oleic acid is a colorless, oily liquid, but the commercial product is reddish-brown and is known as "**red oil**." It is largely used in soap making and in preparing lubricants.

ESTERS

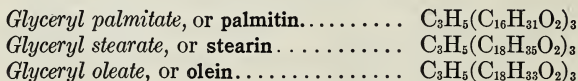
599. Ethyl acetate, $C_2H_5C_2H_3O_2$. Alcohol, which is *ethyl hydroxide*, C_2H_5OH , acts toward acids somewhat like a base. Thus, when acetic acid is warmed with alcohol under suitable conditions, the acid is neutralized and *ethyl acetate* is formed:



Ethyl acetate is a type of an important class of substances called the **esters**. An ester is a compound in which the hydrogen of an acid is replaced by a radical composed of carbon and hydrogen. The simpler esters are colorless liquids slightly soluble in water. They possess an agreeable fruity odor and taste and are employed in imitating the flavors of fruits like bananas, pears, and pineapples.

FATS, OILS, AND SOAPS

600. The fats and oils are *esters* of palmitic, stearic, and oleic acids with glycerine, $C_3H_5(OH)_3$. Since glycerine contains 3 hydroxyl radicals, it requires 3 molecules of the acid to combine with 1 of glycerine, and the resulting ester contains only 1 C_3H_5 radical to 3 acid radicals:



Palmitin and stearin are white solids and are the chief constituents of the hard fats, like tallow and suet. Olein is an

oily liquid, and makes up the bulk of the animal and vegetable oils, like olive oil, corn oil, cottonseed oil, etc.

601. Hydrogenation of fats. From the formulas just given it is plain that the addition of 6 hydrogen atoms would convert the *liquid* olein into the *solid* stearin. When an oil like cottonseed is heated under pressure with hydrogen in presence of finely divided nickel as a catalyst, this addition of hydrogen to olein does in fact take place, and the oil passes into a solid fat. The world-wide shortage of solid edible fats of late years has caused this method of hardening the oils to assume great importance. The cooking fat sold under the name "Crisco" is made from cottonseed oil in this way. Even fish oil, which has a most offensive smell, can be converted into an excellent cooking fat by this process.

602. The soaps. When heated with a solution of sodium hydroxide, a fat yields *glycerine* and the sodium salt of the acid that it contains. According to the fat employed, *sodium palmitate*, *sodium stearate*, or *sodium oleate* is obtained. These three salts resemble each other closely. They are waxy solids which differ from the fats in being soluble in water. They are the chief constituents of the **soaps** of commerce. Their formulas can be obtained by replacing one atom of hydrogen in the corresponding acid by an atom of sodium:

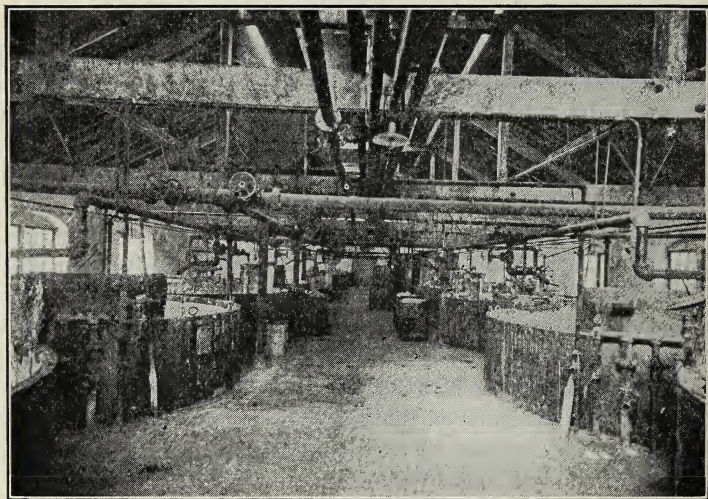
Acid	Soap
Palmitic acid, $C_{16}H_{32}O_2$	Sodium palmitate, $NaC_{16}H_{31}O_2$
Stearic acid, $C_{18}H_{36}O_2$	Sodium stearate, $NaC_{18}H_{35}O_2$
Oleic acid, $C_{18}H_{34}O_2$	Sodium oleate, $NaC_{18}H_{33}O_2$

Because soaps are the chief products, the action of sodium hydroxide upon fats and oils is called **saponification**.

603. Manufacture of soap. Toilet soaps are made from palm oil, cocoanut oil, second-grade olive oil, and tallow oil, and laundry soaps from tallow, bone grease, garbage fat, cottonseed oil, "red oil," which is crude oleic acid from the candle industry, and rosin. A large soap kettle may produce as much

as 150 tons of soap in one boiling. It is heated by steam coils, and there is an open pipe in the bottom by means of which live steam can be blown through the contents for stirring and mixing.

The fat or oil is introduced, together with a dilute solution of sodium hydroxide containing one-fourth of the total sodium hydroxide required for saponification, and the mass is heated



Courtesy of the Procter & Gamble Co.

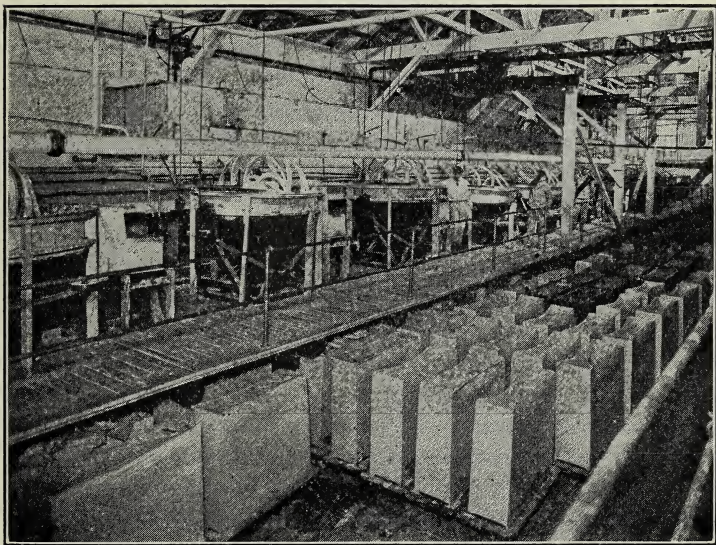
Fig. 282. Tops of soap kettles running through three stories.

and stirred until the oil, instead of swimming upon the surface, breaks up into little globules which are dispersed through the liquid, producing a milky fluid called an **emulsion**.

A stronger solution containing the balance of the sodium hydroxide is now added, and the boiling continued until saponification is complete. Common salt is now added to "salt out" the soap. Since soap is insoluble in salt water, this causes the soap to separate at the top in a liquid layer, which is transferred to a mixing machine called the "crutcher" and

there kneaded for 15 minutes with perfumes, pigments, fillers, or any other materials that are to be incorporated with it.

The liquid is now poured into the "frame," a rectangular box composed of four sheet-iron plates bolted together and mounted on a small truck. Here the soap solidifies. When it has cooled thoroughly, the sheet-iron plates are removed, and



Courtesy of the Procter & Gamble Co.

Fig. 283. Soap crutchers, frames, and stripped blocks.

the block of soap cut into bars by a machine in which steel wires stretched in a frame are forced through the mass. These rough bars are then run through a press which moulds and stamps them, when they are ready to be wrapped and packed.

The watery liquid, called "spent lye," which forms below the soap in the kettle contains the **glycerine**, which amounts to 10 per cent of the weight of the fat or oil employed. Since the boiling point of glycerine is nearly 200° higher than that of

water, the glycerine is easily extracted from the spent lye by fractional distillation.

Floating soaps contain little air bubbles, which are disseminated through the soap by forcing air through it while it is in a pasty condition. *Transparent soaps* are made by dissolving good toilet soap in alcohol and distilling off the alcohol, which is condensed and used again; the soap is left as a transparent jelly, which is moulded and dried. *Naphtha soaps* contain 5 to 10 per cent of naphtha, added in the crutcher. *Scouring soaps* contain 90 per cent of their weight of fine sand, pumice, infusorial earth, powdered glass, or other abrasive rich in silica, cemented together by 10 per cent of soap, which assists the cleansing action. *Liquid soaps* are made with potassium hydroxide instead of sodium hydroxide and are therefore potassium soaps; they are retained in solution by the addition of glycerine or of alcohol. *Shaving powder* is made by drying chips of good toilet soap in a vacuum drier until the water is all gone and the soap becomes brittle, and then pulverizing it. *Soap powders* for kitchen use are obtained by mixing hot melted soap with dry sodium carbonate and water, and drying and pulverizing the mixture.

SUMMARY

An **alcohol** is a compound in which an atom of hydrogen in a hydrocarbon is replaced by the radical **hydroxyl**, OH.

Methyl alcohol, CH_3OH , is commonly called **wood alcohol**. When oxidized it loses two atoms of hydrogen and passes into formaldehyde, CH_2O .

Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, is made from "black strap" molasses, or from starchy materials like corn and potatoes.

Denatured alcohol is made by adding to alcohol poisonous substances which unfit it for use as a beverage.

To each hydrocarbon corresponds an **acid** of the general formula $\text{C}_n\text{H}_{2n}\text{O}_2$.

Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, is the acid of **vinegar**.

An **ester** is produced when an acid interacts with an alcohol.

Glycerine, $C_3H_5(OH)_3$, is obtained from fats and oils as a by-product of the manufacture of soap and candles.

Soaps are composed of *sodium palmitate*, $NaC_{16}H_{31}O_2$, *sodium stearate*, $NaC_{18}H_{35}O_2$, and *sodium oleate*, $NaC_{18}H_{33}O_2$.

EXERCISES

1. Explain the production of wood alcohol, ordinary alcohol, and denatured alcohol.
2. How is formaldehyde made? Describe it and explain its uses.
3. Explain the production of vinegar from cider and other alcoholic liquids.
4. How does acetic acid interact with alcohol? What is an *ester*?
5. Give the formula, properties, and uses of glycerine. How is it obtained?
6. How can oils be converted into solid fats? Why?
7. Write the formulas of palmitin, stearin, and olein.
8. What is the chief constituent of olive oil? Of hard beef tallow?
9. Describe the manufacture of soap.
10. In Columbus, Ohio, the city water supply is softened before distribution through the water mains. What effect would the introduction of this process in other cities have upon the *per capita* consumption of soap?
11. Compare the alcohols with the bases and the esters with the salts.
12. What is the cause of the sweet taste of the fresh juice of apples? What chemical changes occur when the liquid turns first to cider and then to vinegar?
13. Can soap be used satisfactorily with salt water? Why?
14. Is the percentage of oxygen in the fats greater or smaller than the percentage of oxygen in the carbohydrates? How would the difference affect the amount of heat that fats and carbohydrates are capable of yielding when oxidized?

CHAPTER XLIII

EXPLOSIVES AND WAR GASES

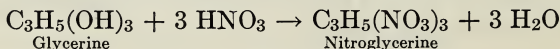
EXPLOSIVES

604. General. An explosive is a solid or liquid substance which can be transformed suddenly into a mass of highly heated gas or vapor. Since the bulk of the gas produced is several thousand times as great as that of the solid or liquid from which it was generated, the change is accompanied by an enormous and forcible increase in volume, taking place in a small fraction of a second, to which the term **explosion** is applied.

So far as total energy is concerned, explosives are far surpassed by the common fuels, and even by many of the substances used as foods. Weight for weight, medium-fat beef contains twice as much energy as does nitroglycerine, chocolate 4 times, and kerosene 8 times as much. The characteristic thing about explosives, however, is that the energy is liberated in a hundred-thousandth of a second or thereabouts, and it is to this that the shattering effects of the explosion are due.

All **high** explosives are compounds containing *nitrogen* along with carbon, hydrogen, and oxygen, and the gases liberated at the moment of detonation are composed of nitrogen, carbon dioxide, and steam. Only a few of the more important explosives can be mentioned here.

605. Nitroglycerine, $C_3H_5(NO_3)_3$. Nitroglycerine is the *ester of glycerine with nitric acid*. It is made by slowly adding glycerine to a cooled mixture of nitric acid and sulphuric acid, the latter being added to take up the water formed in the reaction and thus to prevent the nitric acid from becoming dilute:



The mixture of 2 parts by weight of nitric acid with 3 parts of sulphuric acid is placed in a covered iron tank lined with sheet lead and provided with coils of lead pipe through which cold water circulates, for the temperature must not be allowed to rise above 30°, under penalty of explosion. The glycerine is added in thin streams through a perforated pipe.

The charge is often as much as a ton of glycerine, which yields over 2 tons of nitroglycerine. When the glycerine has all been added, the mixture is allowed to stand, whereupon the nitroglycerine comes to the top and floats on the surface as an oily layer. It is skimmed off and most carefully washed to remove traces of acid, which make it liable to spontaneous explosion.

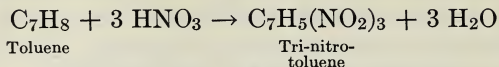
Nitroglycerine is a faint-yellow, odorless oil, with a sweet, burning taste. It is quite poisonous, the effects resembling those of strychnine. Small doses are injected under the skin as a powerful heart stimulant, for instance, in cases of partial suffocation by illuminating gas.

As a result of mechanical shock, friction, or sudden heating, nitroglycerine explodes with great violence. The chief products of the explosion are nitrogen, carbon dioxide, and steam. Nitroglycerine is so sensitive to shock that it cannot be safely transported. This difficulty is avoided by absorbing it in porous infusorial earth (§ 441), making a dry mixture called **dynamite**, which can be transported safely but which can be exploded with certainty at any time by a cap containing *mercuric fulminate*.

In the United States a mixture of wood pulp and sodium nitrate is often used instead of the porous earth as a base to absorb the nitroglycerine. The strongest dynamite of commerce contains three-quarters of its weight of nitroglycerine, but when a milder explosion with less shattering of the rock is desired, as in quarrying building stone or mining coal, a 60-per cent or a 40-per cent dynamite is employed.

606. Tri-nitro-toluene, $C_7H_5(NO_2)_3$. Tri-nitro-toluene, commonly called **T. N. T.**, is made in a similar way to nitro-

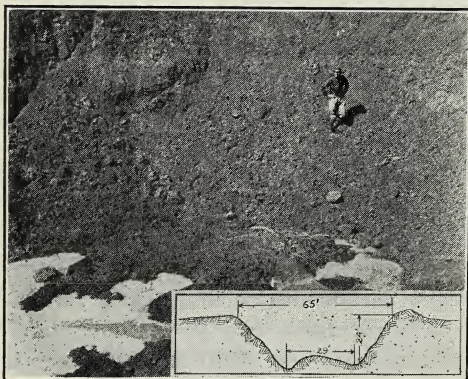
glycerine, by treating the hydrocarbon *toluene*, C_7H_8 , with a mixture of nitric and sulphuric acids:



In this case also, the sulphuric acid is added only to keep the nitric acid *concentrated*.

Tri-nitro-toluene is a yellow, crystalline powder, which can be handled and transported with safety and can even be melted without danger. Like dynamite, it detonates when a cap containing mercuric fulminate is exploded in contact with it.

Tri-nitro-toluene has been adopted by the General Staff of the United States Army as the chief military explosive. For submarine mines, torpedoes, hand grenades, and especially



Courtesy of the Bureau of Ordnance.

Fig. 284. Crater formed by the explosion of 4,000 lb. of tri-nitro-toluene; 1,282 cu. yd. displaced.

for the bursting charge of high-explosive shells, it has displaced all other substances, and enormous quantities were made during the World War and used for these purposes.

607. Nitrocellulose. When cellulose in the form of cotton fibre, pure white paper, or wood pulp is treated with a mixture of concentrated nitric and sulphuric acids, it passes without change of appearance into an explosive known as **nitrocellulose**. Many formulas have been assigned to this substance, but they

have little foundation in fact, for its composition seems to depend upon the way in which it is made. Thus, if cellulose is immersed for half an hour and the acid mixture is free from water, the nitrocellulose produced contains 13.5 per cent of nitrogen, detonates violently with a mercuric-fulminate cap, and is called **guncotton**, whereas if the treatment is briefer and the acid mixture contains a little water, the product contains only 10 per cent of nitrogen, burns energetically but does not detonate, and is known as **collodion**.

Nitrocellulose is made in an iron centrifugal machine with an inner perforated basket. The casing is filled with a mixture of 1 part of nitric acid with 3 parts by weight of sulphuric acid, and the charge of dry cotton, paper, or wood pulp is introduced in small quantities and worked into the acid with an iron fork, the basket being slowly turned. After standing until the chemical change is complete, the acid is run off and the machine rotated rapidly to drain the nitrocellulose. The latter must now be pulped in a hollander (§ 582) and washed with the utmost care to remove retained acid, since if any acid remains in the product spontaneous explosions occur.

608. Nitrocellulose was formerly used for torpedoes and submarine mines, but for these purposes tri-nitro-toluene has displaced it. The chief military use of nitrocellulose is for the production of **smokeless powder**. The action of *acetone*, C_3H_6O , or of a mixture of alcohol and ether, converts nitrocellulose into a plastic mass, which, when passed between rolls, comes out as a transparent, horny sheet. This, cut into leaflets 1 mm. square, is **rifle powder**. For heavy guns the plastic nitrocellulose is run through a press like a macaroni press, which converts it into cylindrical rods having 7 perforations parallel to the axis. The size depends upon the gun, being larger for heavy ordnance. For a 12-in. gun the rod is 3 in. long and $\frac{3}{4}$ in. in diameter.

Nitrocellulose powder of this kind is used by all nations except Great Britain. The British powder ("cordite") con-

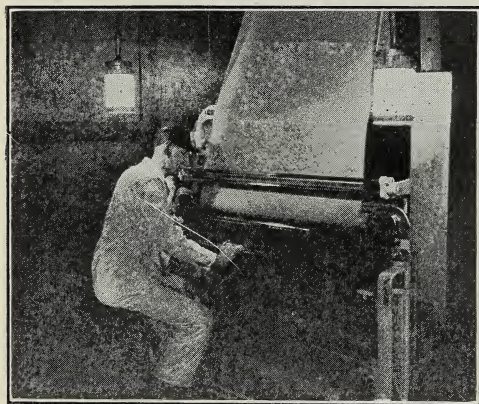
tains 65 per cent of nitrocellulose, 30 per cent of nitroglycerine, and 5 per cent of vaseline. Cordite is safer and more uniform than the nitrocellulose powder, but it has a greater corrosive action on the rifling of the gun. This is a serious disadvantage, for the total life of a heavy gun, *based on the time of actual firing*, is only 3 seconds. After that the piece must be relined.

Smokeless powder alone is used for propelling charges in warfare, black powder being employed only for the bursting charge in shrapnel shells.

609. Collodion dissolves in a mixture of alcohol and ether and is used in surgery to form a coating over wounds. **Lac-**

quers are 3-per cent solutions of collodion in suitable liquids; they are widely used to form a durable protective coating on brass and other metals. **Bronzing liquids**, which consist of lacquers mixed with powdered metals, are employed as radiator paint, etc.

Artificial leather is made by coating canvas with a 10-



Courtesy of the Eastman Kodak Co.

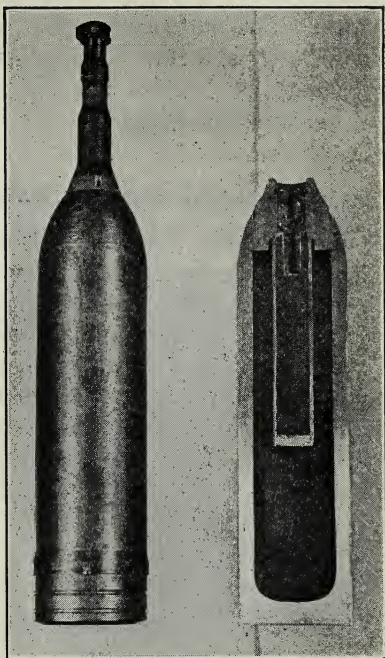
Fig. 285. Celluloid passing through the sensitizing machine for the manufacture of photographic films.

per cent solution of collodion to which dyes are added. The product is often ornamented by passing it through embossing rolls.

Celluloid is manufactured by rolling collodion, made from cotton or white paper, at a gentle heat with half its weight of camphor and a little alcohol in a covered pan. The pure product is transparent and colorless, but it is often rendered white

and opaque by the addition of zinc oxide or is colored with dyes. Warm celluloid is plastic and can be rolled into sheets or moulded into any desired shape. Although it is not explosive, celluloid is highly inflammable. It is largely used as a substitute for ivory, whalebone, horn, and hard rubber. The celluloid is easily detected by rubbing the object vigorously on the coat sleeve, whereupon the odor of camphor is given off. Toughened glass for the windshields of automobiles consists of two sheets of glass cemented to an intermediate sheet of celluloid. The largest use of celluloid is in the production of films for the camera and the motion-picture machine.

610. Mercuric fulminate, $\text{HgC}_2\text{N}_2\text{O}_2$. Mercuric fulminate, often called **fulminating mercury**, is made by dissolving mercury in nitric acid and adding alcohol to the solution. It is very dangerous to make and to handle, especially when dry. Mercuric fulminate is employed solely to detonate other ex-



Courtesy of the Bureau of Ordnance.

Fig. 286. Section of a typical field-gun projectile.

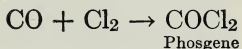
The long nose of the shell carries the percussion fuse. The smaller of the three compartments contains the detonator of mercuric fulminate; the middle compartment, a "booster" charge; and the outer compartment, the bursting charge of trinitro-toluene. The lower end of the shell fits into a brass cartridge case containing the propulsive charge of smokeless powder, which is exploded by a primer of mercuric fulminate.

plosives. Every explosion, whether in warfare or in peace, is brought about by a cap or detonator containing mercuric fulminate. This statement applies, not only to blasting charges, but to pistol and rifle cartridges, to heavy guns, to the bursting charges of shrapnel and high-explosive shells, to torpedoes, and to submarine mines.

THE POISONOUS GASES OF WARFARE

611. General. Gases or vapors to be used for military purposes must be deadly in a proportion of 1 part to 1,000,000 parts of air by volume, and they must be *denser than air*, otherwise they will ascend and be lost. During the World War they were employed either by liberating them from many large cylinders placed in the front-line trenches at a time when the wind blew gently towards the enemy (Fig. 72), or more usually by firing the liquefied gas, in shells containing a small bursting charge, into the enemy lines. Of the 30 or more substances used in this way during the World War, only three of the most important will be mentioned here.

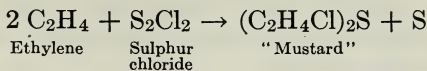
612. Phosgene, COCl_2 , is made by bringing together equal volumes of carbon monoxide and chlorine in presence of charcoal as a catalyst:



It is a colorless, suffocating, highly poisonous gas, easily condensed to a liquid. In addition to attacking the membranes of the nose, throat, and lungs, phosgene depresses and tends to stop the action of the heart.

Chloropicrin, CCl_3NO_2 , is made by heating the well-known yellow dyestuff *picric acid* with bleaching powder. Chloropicrin is a dense liquid which gives off a suffocating vapor. The vapor attacks the eyes, causing copious production of tears, and brings about vomiting by its action upon the stomach. Its action upon the heart resembles that of phosgene.

613. “ Mustard,” $(C_2H_4Cl)_2S$. “ Mustard,” known to the chemist as **di-chlor-ethyl-sulphide**, is made by passing the gas *ethylene*, C_2H_4 , into cold *sulphur chloride*:



“ Mustard ” is a colorless oil, which is not related in any way to the mustard of the household. The name arose from the fact that di-chlor-ethyl-sulphide blisters and burns the skin, producing wounds which heal with great difficulty. The effect of the vapor upon the lungs is to bring about a condition resembling acute pneumonia. As little as 1 volume of the vapor to 70,000,000 volumes of air will so inflame the eyes of a soldier as to make it impossible for him to aim his weapon.

The American **gas mask** is so arranged that all the air that enters the lungs is first filtered through a metal box containing substances that absorb from the air the gases employed in warfare. The box contains layers of a granulated mixture of sodium hydroxide and lime and layers of charcoal made from cocoanut shells, which has a remarkable power of removing many gases and vapors from air.



Courtesy of the Chemical Warfare Service.

Fig. 287. The United States Army gas mask.

SUMMARY

An **explosive** is a substance which can be rapidly transformed into a mass of highly heated gas occupying thousands of times the original volume. When this change occurs in a hundred-thousandth of a second or thereabouts, the substance is known as a **high explosive**.

Nitroglycerine, $C_3H_5(NO_3)_3$, is made by the action of a mixture of nitric and sulphuric acids on glycerine, $C_3H_5(OH)_3$.

Dynamite is composed of nitroglycerine absorbed in porous earth, wood pulp, or sawdust.

Nitrocellulose is prepared by steeping cellulose in a mixture of nitric and sulphuric acids. **Guncotton** and **collodion** are forms of nitrocellulose.

Tri-nitro-toluene, $C_7H_5(NO_2)_3$, is prepared by treating toluene, C_7H_8 , with a mixture of nitric and sulphuric acids.

The most important poison gases of warfare are **phosgene**, $COCl_2$; **chloropicrin**, CCl_3NO_2 ; and "**mustard**" or **di-chlor-ethyl-sulphide**, $(C_2H_4Cl)_2S$.

EXERCISES

1. What is an explosive?
2. Compare the energy of explosives with that of fuels and foods.
3. How is nitroglycerine prepared? What is *dynamite*?
4. What is *nitrocellulose*? Distinguish between *guncotton* and *collodion*.
5. Explain the manufacture of smokeless powder. What is *cordite*?
6. How is tri-nitro-toluene obtained? What are its military uses?
7. Describe the production of mercuric fulminate. What is its only important use?
8. Give the formulas, preparation, and properties of the three chief poison gases of warfare.
9. What absorbent substances are contained in the American gas mask. Does the gas mask protect against carbon monoxide (§ 279)?

10. Hydrocyanic acid, HCN , was tried as a poison gas during the World War but was at once abandoned. Show from its formula that hydrocyanic acid is unsuitable for this purpose.

11. Black gunpowder produces a dense smoke when it explodes, while nitrocellulose powder is smokeless. Why?

12. Illuminating gas burns quietly at the burner, but a mixture of illuminating gas with air explodes violently on the application of a flame. Why?

13. Why are substances like coal dust, charcoal powder, powdered rosin, and even flour dangerously explosive when mixed with air?

14. What is the difference between *high* and *moderate* explosives? Give examples of each.

REVIEW QUESTIONS

What is a *Calorie* (large)? A *calorie* (small)? A *British thermal unit*?

CHAPTER XLIV

FOOD PRODUCTS AND THE DIET

614. Composition of foods. All products used as food are of vegetable or animal origin, and most of them are highly complex mixtures. Nevertheless, the substances in them that are utilized by the body all belong in one of the following five classes:

1. Proteins
2. Fats
3. Carbohydrates
4. Mineral matter
5. Water

615. Proteins. Proteins are highly complex compounds containing carbon, hydrogen, oxygen, nitrogen, and sulphur.¹ Many of them also contain phosphorus, iron, and other elements. The **albumin** of white of egg and the **casein**, or **curd**, of milk are typical proteins.

When heated, the proteins give off an unpleasant smell suggestive of burnt horn or burnt feathers. If a protein is mixed with sodium hydroxide and lime and heated, *ammonia* escapes, which can be recognized by its odor and by the fact that it turns moist red litmus paper *blue*.

When treated with *nitric acid*, a protein turns a bright yellow color, which becomes orange when the nitric acid is neutralized with ammonia.

By means of these three *tests*, proteins can be detected in almost any food product. Among foods that are rich in proteins are lean meat, fish, poultry, eggs, and cheese. The

¹The student can remember these five elements by the syllable CHONS, formed from their symbols.

cereals contain moderate amounts of protein, a larger percentage being present in oatmeal than in most other cereal foods.

The protein of the food is used by the body for the work of construction and repair. Whenever any tissue of the body is worn out and discarded, its place is taken by new tissue built up from the protein of the food. From this it follows that *protein is indispensable in the diet*. When protein is withdrawn, no matter how liberally the other nutrients are supplied, loss of weight begins and symptoms of starvation appear. The protein supply for a full-grown man should not be allowed to fall below 100 grams, which is nearly a quarter pound, per day, and a man doing vigorous muscular work will require more. A woman requires four-fifths as much as a man engaged in a similar occupation.

On the other hand, an excessive amount of protein in the diet is injurious, since it heavily burdens upon the organs of elimination and may lead to disease. Moreover, the proteins are the most expensive constituents of the food, and a diet containing needless quantities of them is wasteful in the extreme.

616. Fats. The chemical nature of the fats has been discussed. The harder fats are chiefly **palmitin** and **stearin**.

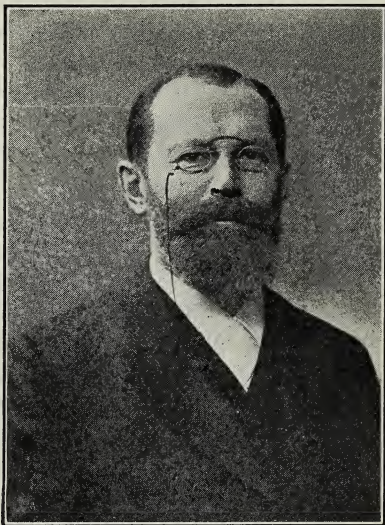


FIG. 288. EMIL FISCHER (1852-1919.)

German chemist, professor of chemistry in the University of Berlin; explained the chemical nature of the proteins and prepared artificially substances quite similar to them; investigated the carbohydrates and obtained synthetically glucose, fructose, and other sugars; synthetically prepared caffeine and many allied substances.

Olive oil and other salad oils consist mainly of **olein**. The soft fats contain all three in intimate mixture. All fats consist for the most part of carbon and hydrogen, with very much smaller percentages of oxygen than are found in proteins and carbohydrates.

This is the explanation of the fact that whereas a gram of protein, when oxidized in the body, gives 4,000 small calories of energy, and a gram of carbohydrate about the same, a gram of fat gives the enormous yield of 9,500 small calories. Because of this large heat of combustion, the fats are especially suited to serve as sources of energy to the body. It is not surprising, therefore, that Eskimos have an appetite for fats which amazes Polar explorers until the latter find themselves, as a result of the climate, beginning to show a similar tendency.

In addition to being directly oxidized to carbon dioxide and water for the production of energy in the forms of heat and motion, fats are stored up in the tissues, to an extent which varies greatly in different persons, as a reserve to be drawn upon when necessary.

The purest fat available for the diet is the oil used for salads, which is practically 100 per cent fat. The different salad oils are nearly equal in nutritive value, the superiority of olive oil being merely in flavor. Milk contains 4 per cent of fat, cheese 30 per cent, and butter and oleomargarine about 85 per cent. Meats as purchased contain abundant fat, but it is usually discarded at the table. However, even lean meat contains some fat. Food products of vegetable origin as a rule contain little fat, but chocolate, olives, and most nuts are exceptionally rich in it. Oatmeal is much richer in fat than are the other cereal foods.

617. Carbohydrates. The occurrence of carbohydrates in food products has already been discussed. In addition to being burned as fuel in the muscles to carbon dioxide and water, carbohydrates often undergo in the body a transformation which cannot be imitated outside it. They are changed

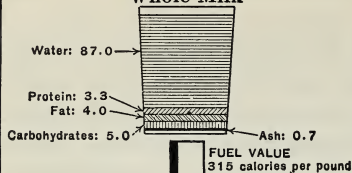
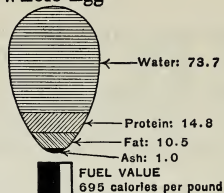
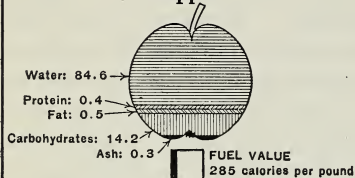
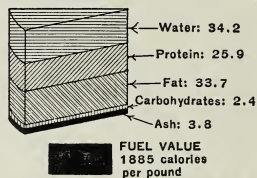
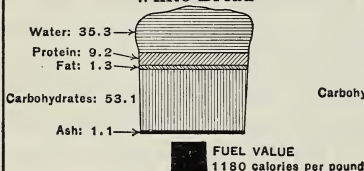
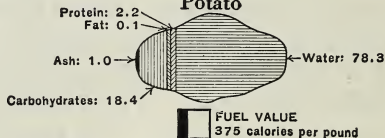
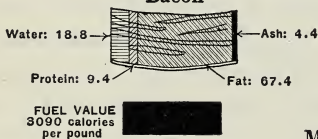
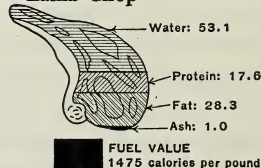
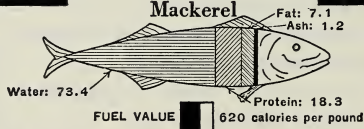
into **fats**, which, in turn, may either be oxidized or stored up as a reserve. The truth of this statement is shown by the fact that the usual plan of fattening stock and poultry for market is to feed them, not upon fats, but upon foods rich in starch. On account of this change of carbohydrates into fats, persons with an excessive tendency to accumulate fat should eat sparingly of sugar and of starchy foods.

Milk and honey are the chief food products of animal origin that are rich in carbohydrates. Among the many vegetable products fitted to supply carbohydrates to the body are raisins, figs, dates, peas, beans, and especially potatoes and the cereal grains. Sugar is the purest form of carbohydrate nourishment, but although wholesome in moderate quantities, it is not fitted to take the place of the foods just mentioned.

618. Mineral matter. The mineral matter of the food remains behind when the food is burned. Its quantity can be determined by heating a weighed quantity of the food product in a platinum dish until combustion is complete and weighing the ash that is left. The function in the body of each variety of the mineral matter of the food has been discussed under the particular elements concerned. A table is given here for review:

MINERAL CONSTITUENTS OF FOODS

Material	Function	Daily Requirement	Suitable Source
COMMON SALT.	Assists formation of HCl in gastric juice	Small	Table salt
CALCIUM.	Nutrition of bones and teeth	0.75 gram	Milk, cereals
PHOSPHORUS..	Nutrition of bones, teeth, and nervous system	1.5 gram	Eggs, milk, cereals, vegetables
IRON.	Nutrition of blood	0.015 gram	Eggs, green vegetables, meat, honey

Whole Milk**Whole Egg****Apple****Cream Cheese****White Bread****Potato****Bacon****Lamb Chop****Mackerel**

Water



Carbohydrates



Protein



Fat



Ash

Fig. 289. Composition of typical food products.

619. Composition of the edible portion of foods. The accompanying table presents the composition of the edible portion of some important food products. The percentages of water, protein, fat, carbohydrate, and ash are given. The column headed "Fuel Value" contains the heat yielded when the fuel is burned, stated in *large Calories per pound* of food. For instance, the statement that the fuel value of lean beef is 838 means that a pound of lean beef, when burned, is capable of producing enough heat to raise the temperature of 838 kg. of water 1°C . These figures are of great interest because they measure the total energy that the different foods will yield when completely oxidized in the body. For certain typical foods the proportion of the various constituents are visualized in Figure 289.

620. Standards of diet. Since both fats and carbohydrates serve as fuel to the body, it is usual, in calculating the food requirements, to state simply the amount of protein and the total number of large Calories. It is understood that both fats and carbohydrates are supplied in the diet.

A full-grown man, in business or practicing a profession that involves little muscular work, requires 100 grams of protein a day, and his food should have a total fuel value of 2,700 Calories, whereas a man at hard muscular work requires 150 grams of protein and a total fuel value of 4,000 Calories. The corresponding values for women can be found by multiplying those for men by 0.8. Children up to the age of 13 require less food than adults, but after that age they require rather more.

The manner in which these facts and the data given in the table on the next page are applied will be seen from the table on page 643, which gives a suitable diet for one day for a business or professional man not doing hard muscular work.

Extensive study has shown that healthy persons, eating without supervision, tend to select a diet that furnishes about 100 grams of protein and 3,000 Calories per day. If a fairly

FOOD VALUES OF IMPORTANT FOOD PRODUCTS

Food Product	Water, per cent	Protein, per cent	Fat, per cent	Carbo- hydrate, per cent	Ash, per cent	Fuel Value, Calories per pound
MEATS						
Beef, lean.....	73.8	22.1	2.9		1.2	838
Ham, lean.....	53.5	20.2	20.8		5.5	1,209
Bacon.....	20.2	9.9	64.8		5.1	2,840
FISH						
Cod, fresh.....	82.6	15.8	0.4		1.2	209
Salmon.....	64.6	21.2	12.8		1.4	582
DAIRY PRODUCTS, ETC.						
Eggs.....	73.7	14.8	10.5		1.0	672
Milk.....	87.0	3.3	4.0	5.0	0.7	314
Butter.....	11.0	1.0	85.0		3.0	3,491
CEREAL PRODUCTS						
Oatmeal.....	7.3	13.3	7.2	67.5	1.9	1,811
Wheat, flour, white.....	11.9	13.3	1.5	72.7	0.6	1,585
Bread, white...	35.3	9.2	1.3	53.1	1.1	1,200
VEGETABLES						
Asparagus.....	94.0	1.8	0.2	3.3	0.7	100
Beans, dried...	12.6	22.5	1.8	59.6	3.5	1,565
Beets.....	87.5	1.6	0.1	9.7	1.1	217
Cabbage.....	91.5	1.6	0.3	5.6	1.0	143
Corn, green....	75.4	3.1	1.1	19.7	0.7	455
Lettuce.....	94.7	1.2	0.3	2.9	0.9	87
Potatoes.....	78.3	2.2	0.1	18.4	1.0	378
Tomatoes.....	94.3	0.9	0.4	3.2	2.1	104
FRUITS						
Apples.....	84.6	0.4	0.5	14.2	0.3	285
Bananas.....	75.3	1.3	0.6	22.0	0.8	447
Oranges.....	86.9	0.8	0.2	11.6	0.5	233
Prunes, dried...	22.3	2.1		73.3	2.3	1,368
Strawberries...	90.4	1.0	0.6	7.4	0.6	169
MISCELLANEOUS						
Almonds.....	4.8	21.0	54.9	17.3	2.0	2,940
Peanuts.....	9.2	25.8	38.6	24.4	2.0	2,490
Olive oil.....			100.0			4,050
Sugar.....				100.0		1,815

TYPICAL ADULT DIET FOR ONE DAY

Food	Weight		Fuel Value, Calories	Protein, grams
	Ounces	Grams		
BREAKFAST				
Bananas.....	3.5	100	100	1.3
Oatmeal.....	1	28	111	4.7
Sugar.....	1	28	111	
Cream.....	2	56	110	1.4
Eggs (2).....	3.5	100	150	13.5
Toast.....	2	56	200	7
Roll.....	1	28	75	2.7
Butter.....	0.5	14	100	0.1
LUNCHEON				
Bluefish.....	4	112	100	22
Potato.....	4.2	120	100	2.6
Rolls.....	2	56	150	5.3
Butter.....	1	28	200	0.2
Milk.....	5	140	100	4.8
Apple pie.....	4	112	300	3.8
DINNER				
Steak.....	4	112	200	27
Potatoes.....	4	112	95	2.5
Corn, canned.....	3.5	100	100	3
Celery.....	4	112	20	1.5
Bread.....	2	56	150	5.3
Butter.....	1	28	200	0.2
Baked apple.....	5.5	154	100	0.6
Cream.....	4	112	220	2.8
Total.....	62.7	1,764	2,992	112.3

constant bodily weight is maintained, and there is no sign of digestive disturbance due to excessive quantities of food, it is likely that the appetite is a safe guide. Loss in weight, undue increase in weight, or indigestion indicates that the food is at fault, and in that case a scientific study of the diet may be of great value in locating the cause of the trouble.

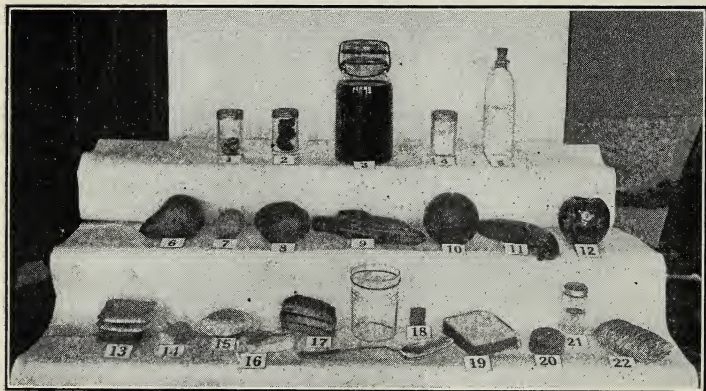


Fig. 290. Food exhibit of hundred-calorie portions.

1, 13 double peanuts; 2, 3 large prunes; 3, 29 oz. clear soup; 4, 4 teaspoonfuls sugar; 5, 5 oz. milk; 6, large pear; 7, large egg; 8, average potato; 9, large ear of corn; 10, large orange; 11, large banana; 12, large apple; 13, 4 Uneda biscuits; 14, 1 cu. in. cheese; 15, $3\frac{1}{2}$ oz. codfish; 16, lamb chop; 17, 3 zweiback; 18, pat butter; 19, slice bread; 20, 2 macaroons; 21, $\frac{2}{5}$ oz. olive oil; 22, shredded wheat biscuit. One tablespoonful = $\frac{1}{2}$ oz. liquid; 1 glass = 8 oz. liquid.

621. Vitamins. In addition to the nutrients and mineral matter already discussed, a healthful diet must supply certain other essential factors known as **vitamins**. These dietary essentials are distributed in very small quantities among various common food products. The exact chemical nature of the vitamins has not been determined, but their identities have been established and their properties discovered by nutrition experiments on a large scale.

Four vitamins have been identified, as follows:

Vitamin A, "fat-soluble," occurs (1) in certain animal fats, notably cream, butter, beef fat, egg yolk, and cod-liver oil, and (2) in the leaves of plants, notably in such leafy vegetables as celery, lettuce, spinach, chard, and beet tops. It is absent from vegetable fats, bolted wheat flour, and polished rice. Deficiency of Vitamin A in the diet results in an infectious eye disease.

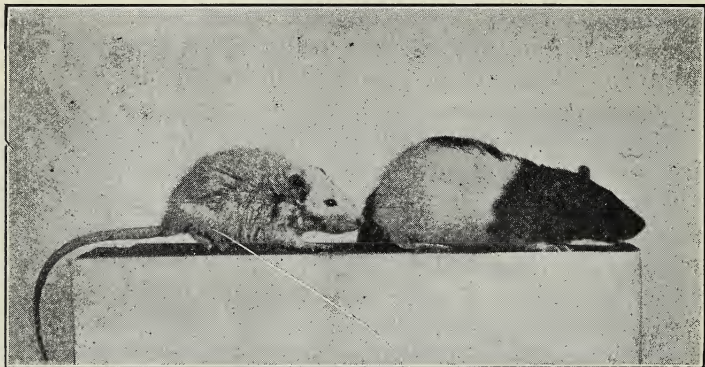
Vitamin B, "water-soluble," is found in almost all natural food products except fats, principally in eggs and the seeds of plants, the germ and bran of cereals, and yeast. Neither bolted wheat flour nor polished rice, however, contains it. Deficiency of Vitamin B results in a type of paralysis known as beri-beri.

Vitamin C occurs in all fresh vegetables and fruits, notably in lemons, oranges, and tomatoes, and less abundantly in milk and fresh meat. It is absent from cereals and dried vegetables. Deficiency of Vitamin C results in scurvy.

Vitamin D occurs in animal fats along with Vitamin "fat-soluble" A but has distinct properties. It is essential to the nutrition of bone, and its absence from the diet is a cause of rickets.

The wide distribution of the vitamins described above indicates that they are liberally supplied by the average American diet. Preserving does not necessarily destroy the vitamins provided the foods are fresh when canned. Professor McCollum says: "It is now well demonstrated that with the diets employed in Europe and America there is no such thing as a 'vitamin' problem other than that of securing an adequate amount of the substance Fat-soluble A"; and he accordingly recommends milk, eggs, and leafy vegetables as "protective foods." Figure 291 presents experimental evidence of the importance of Vitamin A in nutrition. The two rats were of the same age, and their rations from weaning time were exactly alike except in the character of the fats

they contained. The one on the left was given 5 per cent of sunflower seed oil, a very rich vegetable fat. The diet of the one on the right contained 1.5 per cent of butter fat.



Courtesy Prof. E. V. McCollum, from "*The Newer Knowledge of Nutrition*" (Macmillan Co.).

Fig. 291. Effect of vitamin deficiency in the diet.

It is not enough, then, that the diet should be generous, palatable, and wholesome. Serious disturbances of nutrition are likely to result if the diet is not properly balanced to provide the essential vitamins.



Courtesy of Prof. E. V. McCollum.

Fig. 292. Effect of lack of balance in the diet

Figure 292 illustrates the emaciated appearance of a middle-aged rat after being fed about four months on a diet consisting of bolted wheat flour, degerminated corn meal, rice, sugar, starch, pork fat, molasses, sweet potato, and cabbage.

In less than six months such a diet has produced in man the serious and widespread disease pellagra. This diet offers wide variety and consists

of wholesome food products, yet fails to maintain normal nutrition because it contains too little of the *protective foods*, milk, eggs, and the leafy vegetables.

SUMMARY

Proteins are complex compounds of carbon, hydrogen, oxygen, nitrogen, and sulphur. Protein is the chief constructive material of the body. A grown man requires at least 100 grams of protein per day.

Fats and carbohydrates are oxidized in the body to carbon dioxide and water to furnish energy. The diet of a grown man should furnish at least 2,700 Calories each day.

The small percentages of **mineral matter** in food have important functions in the body. This is especially true of *calcium*, *phosphorus*, and *iron*.

Vitamins are essential factors in a healthful diet. Their chemical nature is still unknown. Lack of vitamins is responsible for several so-called "deficiency diseases."

EXERCISES

1. Give three tests by which protein can be detected in food products.
2. Mention six food products rich in protein.
3. What are the effects upon the body of a diet too poor in protein? What effects appear when too much protein is supplied?
4. What is the fuel value of proteins? Of fats? Of carbohydrates?
5. Mention some suitable sources of fat for the diet.
6. Name six food products rich in carbohydrates.
7. How many grams of protein and how many Calories are needed daily by a banker? By a woman employed in a clerical capacity? By a wood chopper?
8. What are the functions of calcium, phosphorus, and iron in the body? What food products are especially rich in these elements?

9. What are the warnings that indicate that the appetite is not acting as a safe guide to the selection of food?

10. What changes in the diet should be made in warm weather? Why does the advent of a "hot wave" cause some loss of appetite, even in perfectly healthy persons?

11. In what way does the Calorie of the dietitian differ from the calorie of the engineer?

12. Why are dietitians so much interested in the amount of heat that food products yield when burned in oxygen?

13. What are *vitamins*? Enumerate the principal sources of the vitamins so far identified.

CHAPTER XLV

RADIUM; THE STRUCTURE OF ATOMS

RADIUM ($Ra = 226$)

622. Occurrence of radium. In notable quantities radium occurs only as an impurity in ores of *uranium*. The chief sources are **pitchblende**, an impure uranium oxide which is found in Austria, and **carnotite**, a yellow mineral containing uranium, vanadium, and lead, which is mined in Colorado and Utah. These minerals contain about 0.3 gram of radium to the ton, which is about 1 part in 5,000,000. Thus the proportion that the weight of the radium bears to the total weight of the ore is about the same as that of *half a second* to a *month*.

In still smaller traces, impossible of extraction, radium is found in the waters of mineral springs (especially in those celebrated for their medicinal value), in most common rocks and soils, and in the air.

623. Preparation and properties. Radium was obtained by Madame Curie in 1910 by the electrolysis of a solution of radium chloride, mercury being used as a cathode. The liberated radium dissolved in the mercury, which was dried and distilled in a current of hydrogen; the mercury vaporized, leaving the radium.

Radium is a silvery metal which resembles calcium. It loses its lustre and turns black in the air, and it liberates hydrogen from water. Radium and all its compounds impart a *red* color to the Bunsen flame.

624. Compounds of radium. Radium is *bivalent*, and its compounds resemble the corresponding compounds of barium. *Radium sulphate*, $RaSO_4$, is a dense, white powder which is

insoluble in water. *Radium chloride*, RaCl_2 , and *radium bromide*, RaBr_2 , are white, crystalline solids resembling common salt in appearance. They are less soluble in water than are the corresponding barium compounds.

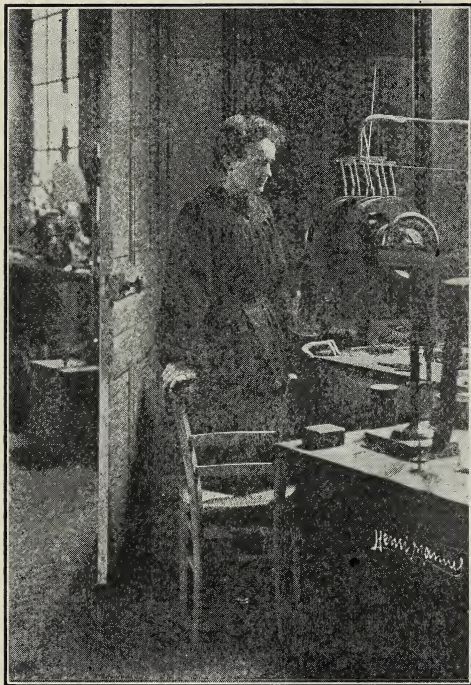


FIG. 293. MARIE SKŁODOWSKA CURIE (1867-).

Polish physicist, professor of physics at the Sorbonne, University of Paris; with her husband, Pierre Curie, took up the pioneer observations of Becquerel on the radioactivity of uranium and in 1910 succeeded in isolating radium with the apparatus shown in the above photograph; shared the Nobel prize for physics with her husband and Becquerel in 1903 and was awarded the Nobel prize for chemistry in 1911.

Radium itself is rarely made, and because of its rapid oxidation in the air, it is unsuitable for practical purposes. In popular language the term "radium" is applied to radium bromide, which is the most important compound of the metal.

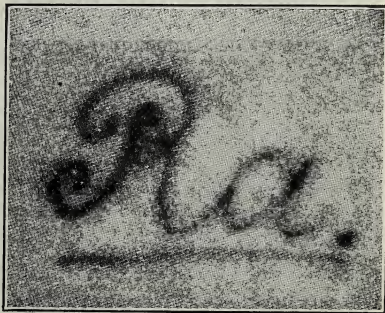
Since the ore contains such a small proportion of radium, its extraction is very difficult. It is for this reason that radium bromide is the most expensive of all chemical products. Its price fluctuates, but it averages

\$100,000 per gram, which is about \$3,000,000 per ounce. Only a few ounces of it have been prepared in pure condition.

625. Radium rays. The name "radium" refers to the fact that all compounds of the metal constantly give off rays. For this reason radium preparations shine in the dark with a pale, bluish light. The rays turn paper brown and glass violet, decompose water into oxygen and hydrogen, destroy the vitality of seeds and microorganisms, and cause severe burns on the hands of chemists who work with strong radium preparations. They were first detected by their effect upon the photographic plate, upon which the radium rays act like light, producing a latent image which appears when the plate is developed. Figure 294 represents a print from a negative obtained by writing upon a photographic plate wrapped in black paper with a glass tube containing radium bromide and then developing the plate. Figure 295 is a photograph of a gram of radium bromide taken in a dark room by the action of its own rays.

We have seen (§ 504) that the rays emitted by uranium cause the air to conduct electricity. This is also true of the radium rays, but since radium is 3 million times as radioactive as uranium, the action upon air is much more energetic. Figure 296 is a tassel made by fastening together thin strips of silk. The tassel has been electrified by rubbing it with a sheet of rubber, and the repulsion of the similar charges causes the strips to diverge as shown. When a strong radium preparation is brought near, the air at once conducts away the charges from the strips, and the tassel collapses.

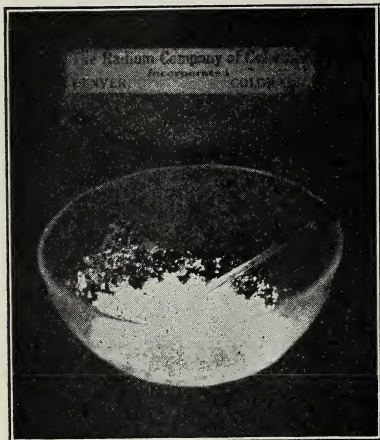
This effect upon air is a convenient *test* for radium. Thus,



After Soddy: "Radioactivity."

Fig. 294. Radium writing on a photographic plate.

to estimate the amount of radium in a mineral, it is sufficient to introduce the weighed specimen into a gold-leaf **electroscope** and measure the time required for the electrified gold leaf to fall through a definite angle. Such a test is inconceivably delicate. It will reveal with certainty quantities of radium so minute as to be imperceptible to the senses and quite impossible to detect by ordinary chemical methods. A diagram of a suitable electroscope is shown in Figure 297.



Courtesy of the Radium Company of Colorado.

Fig. 295. Photograph of a gram of radium bromide taken in a dark room by its own rays.

626. The alpha, beta, and gamma rays. Careful study of the radium rays has shown that they are of three different kinds, which have been named from the first three letters of the Greek alphabet:

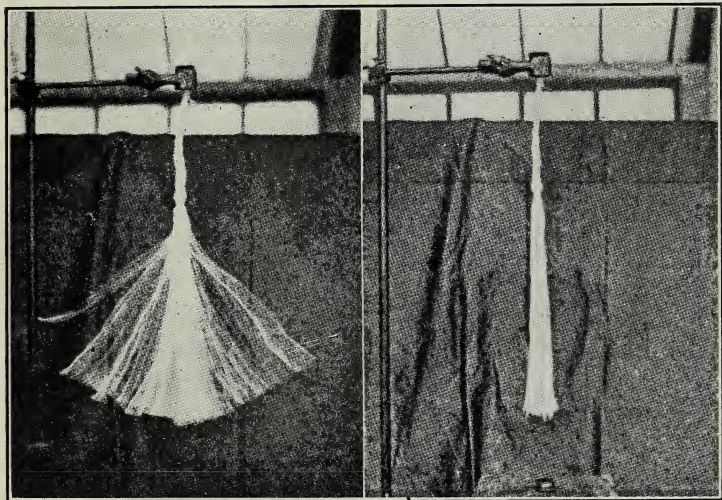
The **alpha rays** are atoms of *helium*, which are pro-

jected out of the radium atom with a speed of 20,000 miles a second. Each helium atom carries with it a double positive charge of electricity, that is, twice the charge that is found upon a hydrogen ion in a solution. The α -rays are the most effective in making the air conduct electricity but have little action upon the photographic plate. They are easily arrested, having a range of less than 9 cm. in air, and a piece of paper, or the thinnest metal foil, stops them completely.

The **beta rays** are **electrons**. The electron is the ultimate particle of negative electricity. Its mass is $\frac{1}{1836}$ of that of the hydrogen atom. The electrons that make up the β -rays are shot out of the radium atoms with a speed which is almost, but

not quite, as great as the velocity of light (186,000 miles per second).

The β -rays are more penetrating than the α -rays. They pass through paper and very thin metal foil almost without loss, but a sheet of lead 1 mm. thick stops them completely. It is chiefly the β -rays that act upon the photographic plate.



After Soddy: "The Interpretation of Radium."

Fig. 296. Electrified silk tassel discharged by radium rays.

The **gamma rays** are not material, but are similar to X-rays. They are, therefore, a vibration in the universal ether, of the same nature as light, but of much greater frequency. The γ -rays are even more penetrating than the β -rays. They pass through an iron plate an inch in thickness with little loss and can still be detected after traversing 8 in. of solid lead.

627. Evolution of heat from radium. Radium preparations are always a little warmer than their surroundings. Measurement shows that a gram of radium evolves each hour 118 small

calories. In other words, radium gives off hourly more than enough heat to raise its own weight of water from the freezing point to the boiling point.

628. Disintegration of radium. Since the atomic weight of helium is 4, a radium atom that shoots out an atom of helium in an α -ray must diminish its own atomic weight of 226 by 4, and the substance that remains must have an atomic weight of 222. This material is a dense, colorless gas which is luminous in the dark. It is termed the **radium emanation**, also called **niton**, Nt:

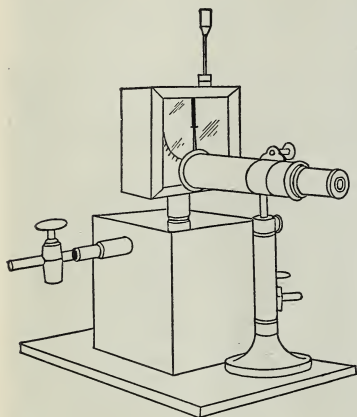
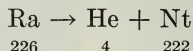
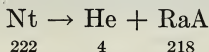


Fig. 297. Electroscope.



Niton also is intensely *radioactive*. Its atom in turn shoots out a helium atom, and the gas turns to a solid which is called **Radium A**, the atomic weight of which is 218:



Thus the disintegration proceeds, each time an atom of helium or an electron being hurled out and an unstable atom being left, until finally, by the continued subtraction of helium atoms and electrons, an atom of *lead* is left, which, not being radioactive, remains without further change.

In a second 1/80,000,000,000 of the atoms of any sample of radium submit to this explosive disintegration. In a year 1/2,450 of the radium would change, and in 1,700 years half of it would disappear, passing into *helium* and *lead*.

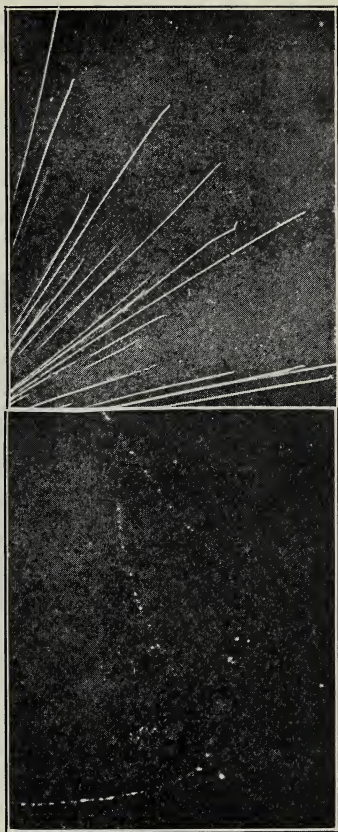
The total energy liberated by a gram of radium during

complete disintegration reaches the enormous figure of 3,680,000 calories, which is more than 250,000 times the energy yielded by a gram of carbon when burned. If the energy of a ton of radium could be controlled and liberated regularly during a period of 30 years, it would suffice, without other fuel, to drive a ship of 15,000 tons displacement at the rate of 15 miles an hour for the whole of that time. The energy locked up in other radioactive elements is equally vast. A ton of uranium contains enough energy to light the city of London for a year.

Unfortunately the liberation of radioactive energy is not under control, and thus far all attempts either to accelerate or to retard the disintegration of radioactive elements have met with complete failure.

The *parent* of radium is *uranium*, the disintegration of which produces radium, helium, and other products. This is the explanation of the fact that radium is found only in minerals containing uranium.

629. Uses of radium. Bombardment with the rays from a radium preparation has been



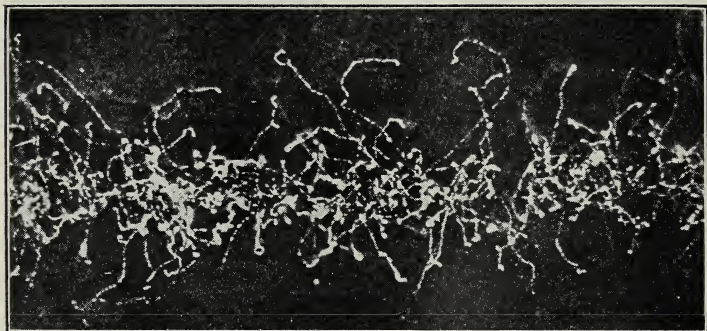
After C. T. R. Wilson.

Fig. 298. Tracks of alpha particles (above) and beta particles (below) in a saturated gas.

The tracks of the particles were made perceptible to the camera by the condensation of water vapor on ions which were formed by their impacts.

used, with some apparent success, for the treatment of cancer and kindred troubles, but physicians are still doubtful of the value of the treatment.

Luminous paint is made by suspending zinc sulphide and a little radium bromide in varnish. The rays from the radium make the zinc sulphide luminous in the dark. Radium paint is applied to the hands of watches and to the figures on the dial, which makes it possible to tell the time at night without



After C. T. R. Wilson.

Fig. 299. Ionization by gamma rays in a saturated gas.

any other source of light. During the World War it was largely used on the dials of measuring instruments on military automobiles and airplanes.

Thorium is radioactive, but much less so than radium, its activity being more like that of uranium. Figure 300 shows the action of the rays from the thorium of a Welsbach mantle upon a photographic plate exposed for 10 days.

THE STRUCTURE OF ATOMS

630. The study of radioactivity, and other researches which lie outside the scope of the present book, have of late, for the first time, enabled scientists to penetrate into the atoms and

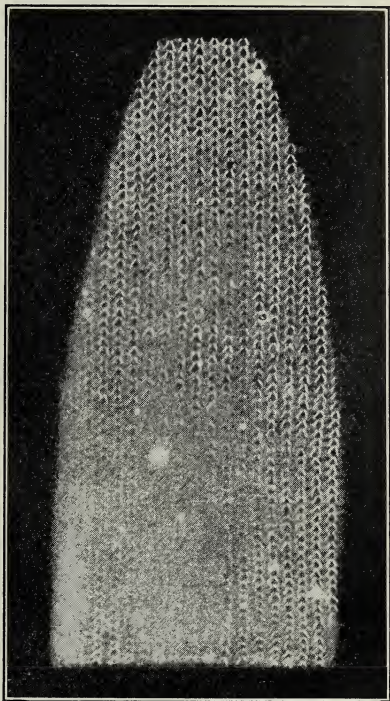
learn about their structure. It has been found that the atoms of all of the elements consist of groups of only two kinds of smaller particles, **electrons** and **protons** or **positive nuclei**.

The **electron** is the ultimate particle of **negative electricity**. It has $\frac{1}{1,760}$ of the mass of the hydrogen atom, and it would require 6 million electrons, laid in contact in a straight line, to equal the diameter of the hydrogen atom. More than 100 billion billion electrons packed in contact would be needed to fill the space occupied by a hydrogen atom.

The **positive nucleus** seems to be the ultimate particle of **positive electricity**. Its *mass* is vastly greater than that of the electron, being *equal* to that of the hydrogen atom. On the other hand, the proton is *still smaller than the electron*, having about $\frac{1}{13}$ the diameter and $\frac{1}{2,000}$ the volume of the latter. Thus, the proton is at

once the *smallest* and the *densest* reality known to science.

The *simplest atom* is that of **hydrogen**. It consists merely of a proton and a single electron whirling around it, held in its course by the electrical attraction, which is enormous at such a small distance. Since the positive and negative charges



Courtesy of the Welsbach Co.

Fig. 300. Photograph of a Welsbach mantle taken by the radioactivity of its thorium.

balance, the atom as a whole is electrically neutral. The **diameter** of the atom is simply that of the circular path of the electron around the nucleus.

If the atom of hydrogen were magnified to a diameter of 200 ft., which is comparable with the dimensions of a cathedral or a large office building, the electron would be about the size of the head of a pin, and the proton would be too small to be seen without a lens. A creature tiny enough to pass into the interior of the hydrogen atom, and possessed of vision like our own, might wander inside it a lifetime without noticing anything but empty space.

The **helium atom** stands next in simplicity. In its center are 4 protons and 2 electrons, and whirling around this central mass, like the moon around the earth, are 2 other electrons.

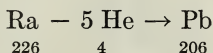
The heavier atoms consist of the same two kinds of particles, but there are more of them. Thus the center of the **silver atom** consists of 108 protons and 61 electrons, crowded together. Whirling about this mass are 47 other electrons, some quite near and some as far as the boundary of the atom. To all intents and purposes the space inside the silver atom would appear empty to a creature capable of examining it, for if the silver atom were magnified to the size of a large classroom, the central mass would be less than $\frac{1}{25}$ of an inch in diameter, and the revolving electrons would be invisible to the unaided eye.

631. Atomic numbers. Here we encounter a new classification of the elements, based upon **atomic numbers**, instead of *atomic weights*, and nearly, but not quite, identical with the periodic classification. The atomic number of an element is the excess positive charge of the atomic nucleus, or, what is the same thing, the number of electrons whirling around the nucleus. Thus, the atomic number of hydrogen is 1, that of helium 2, and that of silver 47, while uranium, the end of the series, receives the atomic number 92.

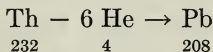
It is the number of outlying electrons that determines the

chemical character of an element. In other words, the properties of the elements are dependent upon the atomic numbers, rather than upon the atomic weights. Thus, the atomic number of *lead* is 82, which signifies that there are 82 electrons whirling about a nucleus the excess positive charge of which is 82 units. Let us leave the 82 external electrons undisturbed and remove 1 electron and 1 proton from the central mass. The resulting atom would have an atomic *weight* of only 206, but its atomic *number* would still be 82, and it would still be lead.

This kind of lead is the final product of the disintegration of radium:



Still another variety of lead is the end-product of the radioactive disintegration of thorium:



Elements that have the same atomic numbers but slightly different atomic weights are called **isotopes**. Isotopes are identical in chemical conduct, and are, therefore, inseparable by chemical methods. Ordinary lead is probably a mixture of the two isotopes just mentioned.

It is probable that the atomic weights are really whole numbers. The uneven numbers obtained by experiment are due to the presence of two or more isotopes in the material investigated. Details for some of the elements are given in the following table. The student should notice that in all cases in which the atomic weight deviates much from a whole number, the deviation is accounted for in this way. Very *slight* deviation, as in the case of iodine, is accounted for by an actual *loss of mass*, which results from the crowding together of the protons and electrons in the atomic nucleus.

b

TABLE OF ELEMENTS AND ISOTOPES

Professor Aston

Element	Atomic Number	Atomic Weight	Number of Isotopes	Atomic Weights of Isotopes
HYDROGEN...	1	1.008	1	1.008
HELIUM.....	2	4.0	1	4.0
BORON.....	5	10.9	2	11, 10
NEON.....	10	20.2	2	20, 22
SILICON.....	14	28.3	2	28, 29
CHLORINE...	17	35.46	2	35, 37
ARGON.....	18	39.9	2	40, 36
BROMINE....	35	79.92	2	79, 81
IODINE.....	53	126.92	1	127
MERCURY...	80	200.6	4	197, 200, 202, 204

Carbon, nitrogen, oxygen, fluorine, phosphorus, sulphur, and arsenic, all of which have even numbers for their atomic weights, give no evidence of the existence of any isotopes.

632. Metals and non-metals; valence. The atom of the metals readily lose one electron or more, which leaves the metal-atom positively charged. Hence, *metals are good conductors of electricity*, for the free electrons carry the electric current. A univalent metal, like sodium, easily loses a single electron, and its atom is left with a unit positive charge. The atom of a bivalent metal, like zinc, readily loses 2 electrons, and remains with a double positive charge, and so on.

The atoms of the non-metals readily accept extra electrons and become negatively charged, the univalent atoms taking up 1 additional electron, the bivalent atoms 2, and so on. Thus the valence of an element is determined by the number of electrons lost or gained by its atom. Since there are no free electrons in a non-metal, the *non-metals are non-conductors of the electric current*. When chlorine is brought into contact with sodium, each chlorine atom takes an electron from a sodium atom, and the electrostatic attraction between the

negatively charged chlorine atoms and the positively charged sodium atoms brings about chemical union to sodium chloride. Among the atoms of the elements, those of *fluorine* are the most eager to pick up an extra electron, while those of *cæsium* are the most ready to lose one. Hence, fluorine is the most active of the non-metallic elements, while *cæsium* is chemically the most perfect metal.

633. The alchemists worked vainly for centuries at the problem of converting lead and other base metals into gold. They failed, and the failure led gradually to the idea that the atom of gold was simply a little mass of *gold*, and was made, therefore, of a totally different substance from the atom of lead or of any other element. The atoms of each element were supposed to be, in the same way, fundamentally distinct from those of the other elements, and hence to transform one element into another was regarded as an impossibility.

This view of the structure of the atoms was of great value to chemistry for more than a century, but the facts of radioactivity have forced us to abandon it. Uranium passes very slowly into other elements, two of which are helium and radium, and radium, in turn, decays, changing finally into helium and lead. Both the atom of lead and that of gold are composed of electrons and protons, and the problem of converting lead into gold is simply the problem of converting the lead arrangement of electrons and protons into the gold arrangement.

However, not the slightest progress has yet been made in this direction, and there is good reason to believe that the task of transmuting the elements will be one of surpassing difficulty. One thing is certain, that if scientists ever succeed in transforming one element into another, the amount of energy released at the same time will be so large that it will far exceed in value the gold or other material product of the transmutation. If a pound of lead could be transformed into gold, the energy set free would probably be several million times as great as that liberated by the explosion of an equal weight of nitroglycerine.

In fact, if man ever succeeds in tapping the enormous latent supplies of energy in the atoms, coal, petroleum, gas, and all other sources of power will become, at one stroke, superfluous.

SUMMARY

Radium is found only in minerals containing uranium, especially in *pitchblende* and *carnotite*.

Radium is a combustible metal resembling barium, and its compounds resemble those of barium.

Radium bromide, RaBr_2 , is the most important radium compound, and it is commonly called "radium."

Radium and all of its compounds are **radioactive**. They continually emit three distinct kinds of rays:

The **alpha rays** are *atoms of helium*, shot out with a speed of 20,000 miles a second.

The **beta rays** are *electrons*, projected almost with the speed of light.

The **gamma rays** are *X-rays*, emitted with the speed of light.

The emission of the rays is due to the fact that each second some of the radium atoms become unstable and explode. This is only a small fraction of the total number present.

Uranium is radioactive, and radium is one of the products of its disintegration.

The **final products** of all radioactive changes seem to be **helium** and **lead**.

The atoms of the elements are all composed of two kinds of smaller particles, **electrons** and **protons**.

EXERCISES

1. What are the chief commercial sources of radium?
2. Why is radium found only in ores containing uranium?
3. Mention some effects of the radium rays.

4. What is the radium *emanation*? Explain the distinction between the emanation and the rays.
5. Explain the nature of the three kinds of rays.
6. What is meant by *radioactive disintegration*.
7. Explain the constitution of the hydrogen atom. Of the helium atom.
8. Discuss the structure of atoms in general, using the silver atom as an example.
9. To what extent has modern science realized the attempts of the alchemists?
10. If transmutation of the elements into each other were possible, would the actual work be safe or dangerous? Why?
11. What are some of the differences between radioactive changes and ordinary chemical changes?
12. The radiochemist applies to *lead* the term Radium G. What does this mean?
13. In all ages there have been thinkers who held that all material things are forms of one universal substance. To what extent has this belief been verified?

APPENDIX

LOGARITHMS

Natural Number											Proportional Parts								
	0	1	2	3	4	5	6	7	8	9	1 2 3			4 5 6			7 8 9		
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 8 12	17 21 25	29 33 37						
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 11	15 19 23	26 30 34						
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 10	14 17 21	24 28 31						
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 6 10	13 16 19	23 26 29						
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9	12 15 18	21 24 27						
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 8	11 14 17	20 22 25						
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8	11 13 16	18 21 24						
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2 5 7	10 12 15	17 20 22						
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7	9 12 14	16 19 21						
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7	9 11 13	16 18 20						
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19						
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18						
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17						
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17						
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16						
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15						
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15						
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14						
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14						
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13						
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13						
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12						
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12						
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12						
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11						
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11						
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11						
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10						
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10						
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10						
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10						
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9						
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9						
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9						
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9						
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9						
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8						
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8						
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8						
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8						
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8						
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8						
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7						
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7						
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7						
	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9						

LOGARITHMS

Natural Number	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7921	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9325	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9375	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

CENTIGRADE-FAHRENHEIT CONVERSION TABLE

C.°	0	10	20	30	40	50	60	70	80	90	
-200	F. -328	F. -346	F. -364	F. -382	F. -400	F. -418	F. -436	F. -454	F.	F.	
-100	-148	-166	-184	-202	-220	-238	-256	-274	-292	-310	
-0	+32	+14	-4	-22	-40	-58	-76	-94	-112	-130	
0	32	50	68	86	104	122	140	158	176	194	
100	212	230	248	266	284	302	320	338	356	374	C.° 1
200	392	410	428	446	464	482	500	518	536	554	F.° 2
300	572	590	608	626	644	662	680	698	716	734	3
400	752	770	788	806	824	842	860	878	896	914	4
500	932	950	968	986	1,004	1,022	1,040	1,058	1,076	1,094	5
600	1,112	1,130	1,148	1,166	1,184	1,202	1,220	1,238	1,256	1,274	6
700	1,292	1,310	1,328	1,346	1,364	1,382	1,400	1,418	1,436	1,454	7
800	1,472	1,490	1,508	1,526	1,544	1,562	1,580	1,598	1,616	1,634	8
900	1,652	1,670	1,688	1,706	1,724	1,742	1,760	1,778	1,796	1,814	9
1,000	1,832	1,850	1,868	1,886	1,904	1,922	1,940	1,958	1,976	1,994	10
1,100	2,012	2,030	2,048	2,066	2,084	2,102	2,120	2,138	2,156	2,174	
1,200	2,192	2,210	2,228	2,246	2,264	2,282	2,300	2,318	2,336	2,354	
1,300	2,372	2,390	2,408	2,426	2,444	2,462	2,480	2,498	2,516	2,534	
1,400	2,552	2,570	2,588	2,606	2,624	2,642	2,660	2,678	2,696	2,714	
1,500	2,732	2,750	2,768	2,786	2,804	2,822	2,840	2,858	2,876	2,894	
1,600	2,912	2,930	2,948	2,966	2,984	3,002	3,020	3,038	3,056	3,074	
1,700	3,092	3,110	3,128	3,146	3,164	3,182	3,200	3,218	3,236	3,254	F.° 1
1,800	3,272	3,290	3,308	3,326	3,344	3,362	3,380	3,398	3,416	3,434	2
1,900	3,452	3,470	3,488	3,506	3,524	3,542	3,560	3,578	3,596	3,614	3
2,000	3,632	3,650	3,668	3,686	3,704	3,722	3,740	3,758	3,776	3,794	4
2,100	3,812	3,830	3,848	3,866	3,884	3,902	3,920	3,938	3,956	3,974	5
2,200	3,992	4,010	4,028	4,046	4,064	4,082	4,100	4,118	4,136	4,154	6
2,300	4,172	4,190	4,208	4,226	4,244	4,262	4,280	4,298	4,316	4,334	7
2,400	4,352	4,370	4,388	4,406	4,424	4,442	4,460	4,478	4,496	4,514	8
2,500	4,532	4,550	4,568	4,586	4,604	4,622	4,640	4,658	4,676	4,694	9
2,600	4,712	4,730	4,748	4,766	4,784	4,802	4,820	4,838	4,856	4,874	10
2,700	4,892	4,910	4,928	4,946	4,964	4,982	5,000	5,018	5,036	5,054	11
2,800	5,072	5,090	5,108	5,126	5,144	5,162	5,180	5,198	5,216	5,234	12
2,900	5,252	5,270	5,288	5,306	5,324	5,342	5,360	5,378	5,396	5,414	13
3,000	5,432	5,450	5,468	5,486	5,504	5,522	5,540	5,558	5,576	5,594	14
3,100	5,612	5,630	5,648	5,666	5,684	5,702	5,720	5,738	5,756	5,774	15
3,200	5,792	5,810	5,828	5,846	5,864	5,882	5,900	5,918	5,936	5,954	16
3,300	5,972	5,990	6,008	6,026	6,044	6,062	6,080	6,098	6,116	6,134	17
3,400	6,152	6,170	6,188	6,206	6,224	6,242	6,260	6,278	6,296	6,314	18
3,500	6,332	6,350	6,368	6,386	6,404	6,422	6,440	6,458	6,476	6,494	
3,600	6,512	6,530	6,548	6,566	6,584	6,602	6,620	6,638	6,656	6,674	
3,700	6,692	6,710	6,728	6,746	6,764	6,782	6,800	6,818	6,836	6,854	
3,800	6,872	6,890	6,908	6,926	6,944	6,962	6,980	6,998	7,016	7,034	
3,900	7,052	7,070	7,088	7,106	7,124	7,142	7,160	7,178	7,196	7,214	
C.°	0	10	20	30	40	50	60	70	80	90	

EXAMPLES: 1,347° C. = 2,444° F. + 12.6° F. = 2,456.6° F.
 3,367° F. = 1,850° C. + 2.78° C. = 1,852.78° C.

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